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# **Curing Behavior and Bonding Performance of Wood Adhesives under High-Pressure Steam\***

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\* This review article is the abstract of the doctor thesis by the author (Kyoto University, 1996).

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## Introduction

In the production of wood based materials, the pressing is one of the most important processes for both productivity and quality of products. Instead of using conventional hot-platen heating, recently, several pressing methods have been developed and introduced<sup>1)</sup>. In particular, steam-injection pressing method in which high-pressure steam is injected into

wood materials during pressing, has received much attention all over the world<sup>2)</sup>. Many researches on wood based materials using steam-injection pressing have been reported<sup>3-5)</sup>. In the steam-injection pressing, as the wood materials are exposed to high-pressure steam, the temperature of wood elements rises immediately compared to hot-platen pressing, which accelerates the cure of resin adhesives. As a result, the pressing time becomes shorter than by conventional hot-platen pressing<sup>2)</sup>.

Almost all of the adhesives currently used to manufacture wood materials are formaldehyde resin adhesives. It is very important to know the curing characteristics of adhesives during the pressing processes. However, researches on adhesives have been done mainly on the assumption that wood products are manufactured by hot-platen pressing. Though some researchers<sup>6-10)</sup> have reported the effect of high-pressure steam on curing of adhesive, they did not discuss in detail. Consequently, the steam-injection pressing conditions for the manufacture of wood composite materials have been decided empirically so far. Therefore, the basic information on curing process and bonding performance of adhesives under high-pressure steam is necessary for the development of the steam-injection pressing technology.

The purpose of present study is to clarify the curing behavior and to establish the optimum bonding conditions of wood adhesives, particularly PF and UF resins, under high-pressure steam. In the first place, the curing mechanisms of PF and UF resins under high-pressure steam were discussed. That is, resins treated by steam-injection heating and hot-platen heating were analyzed and compared with each other using techniques such as fourier transform infrared spectroscopy (FT-IR), solvent extraction and dynamic mechanical analysis (DMA). In the second place, based on the obtained results, the bonding performance and optimum bonding conditions of each resin under high-pressure steam were investigated.

## **Part 1 Curing Behavior of Phenol-Formaldehyde Resin under High-Pressure Steam**

### **1.1 Introduction**

The curing reactions of PF resin greatly depend on the formaldehyde/phenol mole ratio, pH of the resin, and the reaction temperature. As shown in Fig. 1.1, the cure of PF resin involves the substitution reactions of the methylol reactive group at a reactive site of an aromatic ring yielding a methylene linkage between two aromatic rings (Reaction 1). It also can be speculated that a substitution reaction by a methylol reactive group of another methylol hydroxyl group yielded a methylene ether linkage (Reaction 2). However, the primary reaction under alkaline conditions is considered to be the formation of a methylene linkage. From extensive investigation, minor ether-forming reaction was found to occur,

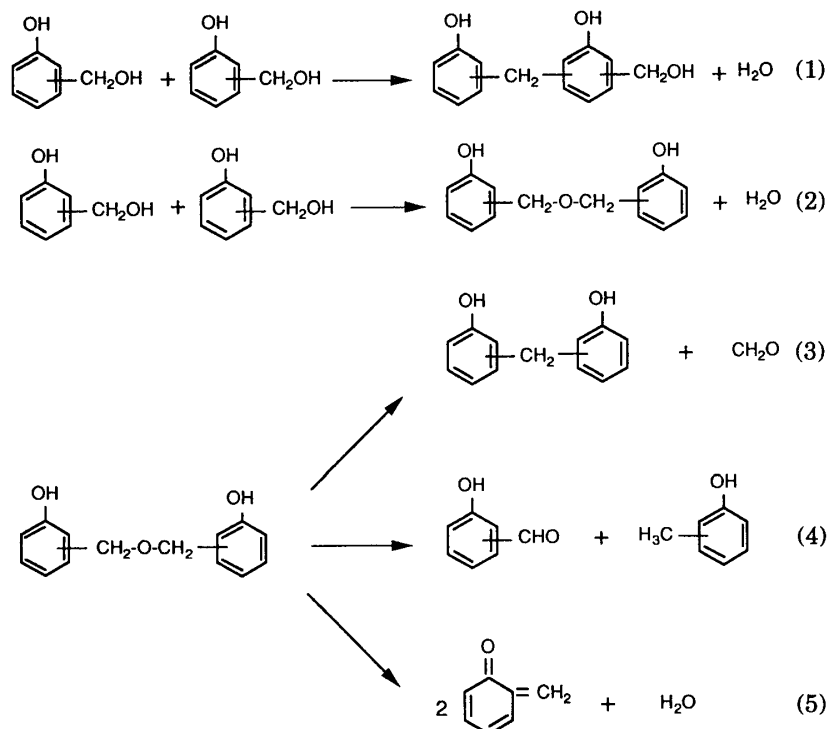


Fig. 1.1. Curing reactions of resol-type phenol formaldehyde resin.

and methylene ether linkages formed seem to break down with longer periods of cure or higher cure temperatures (140–170°C)<sup>11)</sup>. The three possible products of decomposition of the ether linkage that have been received as represented by Reactions (3) to (5). That is, the ether linkage splits to give a methylene bridge (Reaction 3) or decompose to give a phenolic aldehyde and methylated phenol (Reaction 4) or decompose to form a quinone methide structure (Reaction 5). Reaction (3) however, is considered the main reaction, and Reactions (4) and (5) are considered to be side reactions<sup>12)</sup>.

The objective of this part is to reveal the curing behavior of PF resin under high-pressure steam chemically and physically. The section 1.2 dealt with the curing behavior of PF resol resin under high-pressure steam, using a specially designed reaction cell<sup>8)</sup>. First, using 2-hydroxybenzyl alcohol as a model compound, the differences between the curing reactions under hot-platen heating and under steam-injection heating were observed. Second, the PF resins heated by both two heating methods were analyzed by FT-IR, <sup>13</sup>C-NMR and solvent extraction.

The section 1.3 dealt with the curing process and the effects of the pre-heating of PF resin under both heating conditions measured by DMA. In addition, the dynamic mechanical curing index, indicating the degree of dynamic mechanical cure for the pre-heated PF resins, was proposed, and its behaviors were evaluated.

## 1.2 Chemical analysis of curing behavior

### 1.2.1 Materials and methods

#### (1) Materials

The aqueous PF resol resin was prepared by initially reacting 94 g of phenol (P) with 162 g of formaldehyde solution (F), to give an F/P molar ratio of 2.0. Thirty-two grams (32 g) of 50% NaOH solution was also added as a catalyst, to give a NaOH/P ratio of 0.4. The mixtures were heated gradually until 75°C for 60 min and then were heated for 5 h at 76°C. Upon reaching a viscosity of 1.1 poise, the solution was cooled to 20°C for 90 min. The properties of PF resin were shown in Table 1.1. The model compound, 2-hydroxybenzyl alcohol (Aldrich Chem. Co.) was dissolved in a NaOH solution. The solution had a 46% solid content with pH 11, as well as PF resol resin.

#### (2) Heating methods

Steam-injection heating was done by using a specially designed experimental apparatus as shown in Fig 1.2<sup>8)</sup>. Each adhesive was weighed and contained in a polytetrafluoroethylene film bag. The amounts of resin were about 0.2 g for FT-IR and about 2.5 g

Table 1.1. Properties of PF resin.

pH	11
Viscosity (25°C)	0.088 (Pa·s)
Specific gravity (25°C)	0.177
Molecular weigh ( $\bar{M}_n$ )	705
Gelation time (boiling water)	27.27 (min)
Non-volatile component (135°C, 1 h)	45.8 (%)

Legend:  $\bar{M}_n$ : Number average molecular weight. Note: Molecular weight ( $\bar{M}_n$ ) obtained from polyethylene glycol calibration curve of gel permeation chromatography.

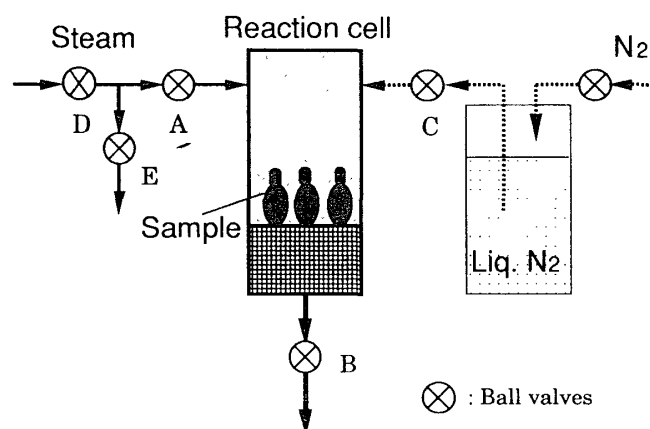


Fig. 1.2. Apparatus for heating adhesives under high-pressure steam.

for other analyses. The procedure followed the suggestion of Subiyanto *et al.*<sup>8)</sup>. That is, the polytetrafluoroethylene film bag was tied loosely with wire immediately before putting them in the reaction cell so as to prevent the condensed water from penetrating into the bag and also to prevent the bag from bursting from adhesive reaction or boiling. The temperature inside the reaction cell was recorded at certain time intervals. After a few seconds of warming, condensed water was drained in the steam line by opening the ball-valves D and E. Valve E was then closed and a high-pressure steam was injected into the reaction cell by opening valve A. The target heating temperature was achieved by controlling steam pressure from a steam generator. The heating temperatures (steam pressure) were 160°C (0.63 MPa) with steam-injection times from 10 s to 60 min. After steam injection for the scheduled time, valve A was closed and valve B was opened to reduce steam pressure for a few seconds followed immediately by opening valve C to inject liquid nitrogen (Liq. N<sub>2</sub>) into the reaction cell until the adhesives were frozen. Frozen samples were taken out and kept in a freezer at -20°C until analysis was done.

In hot-platen heating, about 0.2 g (for FT-IR) and 2.5 g (for other analyses) of resin contained in separate polytetrafluoroethylene films were placed between the platens (about 2.5 mm opening between upper and lower platens). The heating temperatures were 160°C with heating times from 10 s to 60 min. After the resin was heated for the scheduled time, it was dipped in liquid nitrogen in order to stop the curing reaction. Then, all the samples were kept in a freezer set at -20°C.

### (3) FT-IR and solvent extraction

The frozen samples were vacuum-dried and ground to a powder before analysis. Infrared absorbance spectra was obtained on a Nihon Bunko FT/IR-7000 using KBr pellet technique. To observe the reaction quantitatively, intensity ratio method was used for each obtained spectrum.

Solid-state <sup>13</sup>C-NMR spectra was obtained at 50.3 MHz with a Varian XL-200 spectrometer equipped with a CP-MAS probe made by Doty Scientific Inc.

A heat treated and pulverized (less than 20 mesh) dry sample weighing 2.5 g was extracted for 24 h with methanol in a Soxhlet extractor. After that, the amount of residue was determined, and the proportion of the insoluble matter was calculated.

## 1.2.2 Results and discussion

### (1) Curing reaction of 2-hydroxybenzyl alcohol

The curing reaction of 2-hydroxybenzyl alcohol as a model compound was observed. Fig. 1.3 shows the IR spectral changes of this compound under hot-platen heating (A) and steam-injection heating (B). These spectra were measured after heating the samples at 160°C for 1 min (a), 5 min (b), and 20 min (c) respectively.

In hot-platen heating (A), the curing process of this compound was characterized in a previous report as follows<sup>13)</sup>: The intensity of the band of the compound heated for 30 min

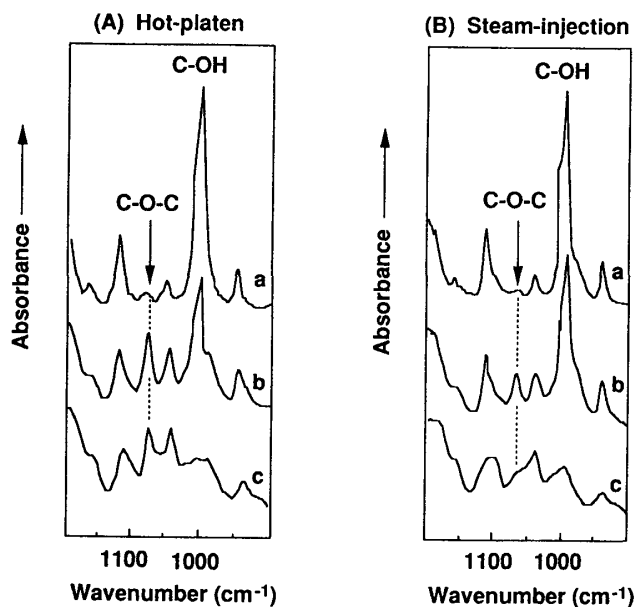


Fig. 1.3. Infrared spectra of 2-hydroxybenzyl alcohol during hot-platen heating (A) and steam-injection heating (B) at 160°C. Legend: (a) 1 min, (b) 5 min, (c) 20 min.

at 160°C due to the C-OH stretching vibrational mode at about 995  $\text{cm}^{-1}$ , decreases, and the intensity of the band due to the C-O-C stretching vibrational mode at about 1070  $\text{cm}^{-1}$  also decreases. In this study, the band due to the C-OH mode at about 995  $\text{cm}^{-1}$  rapidly decreased, and that due to the C-O-C mode at about 1,070  $\text{cm}^{-1}$  increased with increasing heating time under hot-platen heating. Besides Reaction (1) as shown in Fig. 1.1, the Reaction (2) could occur at 160°C for 20 min under hot-platen heating.

In steam-injection heating (B), the band at about 995  $\text{cm}^{-1}$  decreased, and the band at about 1,070  $\text{cm}^{-1}$  increased and then decreased with increasing heating time. As the formation and decomposition of ether structure were observed, Reaction (2)–(5) were considered to occur in steam-injection heating. However, the formation of the peaks arising from aldehyde group and quinone methide structure were not observed in the IR chart. Therefore, besides Reaction (1), Reaction (2) and (3) would occur at 160°C for 20 min under steam-injection heating. That is, in the curing of 2-hydroxybenzyl alcohol under steam-injection heating at 160°C, the ether linkage was thought to decompose rapidly.

#### (2) Curing behavior of PF resin examined by FT-IR

Based on previous works on IR measurements of PF resin<sup>14,15)</sup>, the bands of primary interest are about 1,010  $\text{cm}^{-1}$  for C-O stretch of methylol ( $\text{CH}_2\text{-OH}$ ), 1,050  $\text{cm}^{-1}$  for C-O stretch of ether (C-O-C), and 1,650  $\text{cm}^{-1}$  for C=O stretch of carbonyl (C=O). To observe the curing behavior of the resin quantitatively, as well as to compare the heated resins which were obtained by the two heating methods, the ratios of the intensities of the bands at about 1,010, 1,050, and 1,650  $\text{cm}^{-1}$  to that of the aromatic C=C stretching



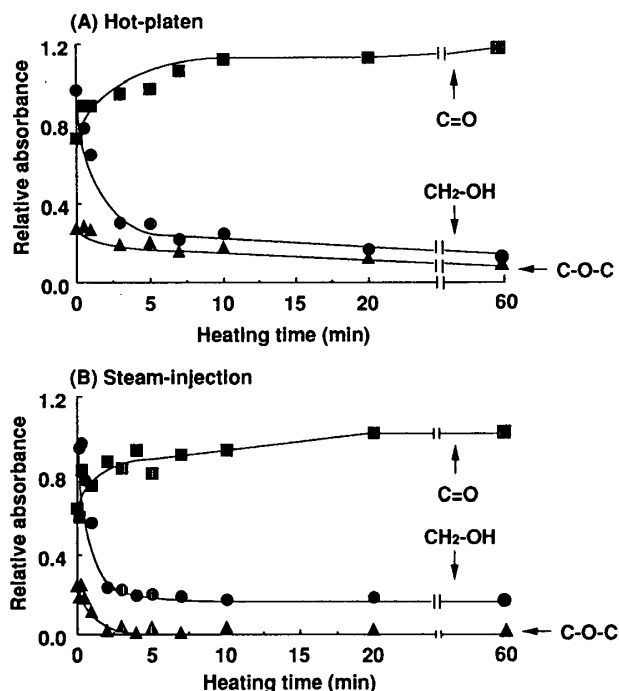


Fig. 1.4. Infrared changes of PF resin during hot-platen heating (A) and steam-injection heating (B) at 160°C. Legend: ■: 1,650  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$ , ●: 1,010  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$ , ▲: 1,050  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$ .

vibrational mode at about 1610  $\text{cm}^{-1}$  were plotted against the heating time<sup>16)</sup>. The results are shown in Fig. 1.4. By hot platen heating (A) in Fig. 1.4, the ratio of 1,650  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  gradually increased with increasing heating time, while 1,010  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  rapidly decreased for 3 min and then gradually decreased. The ratio of 1,050  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  slightly decreased over the entire heating time. By steam-injection (B), 1,650  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  rapidly increased and soon reached a constant value within 20 min, while 1,010  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  decreased rapidly in the early stage (to 3 min), then maintained a constant value. 1,050  $\text{cm}^{-1}$ /1,610  $\text{cm}^{-1}$  also rapidly decreased, and finally it almost kept its value of 0.

Fig. 1.5 shows the  $^{13}\text{C}$ -NMR spectra of the hot-platen heated resin (A) and that of the steam-injection heated resin (B) at 160°C for 20 min. The structural assignments were derived from the literature<sup>17,18)</sup>. In hot-platen heated resin (A), about 62 ppm of methylol and about 73 ppm of ether linkage were observed. In steam-injection heated resin (B), these peaks had weaker intensities than that in hot-platen heating, especially, the peak of ether linkage. This tendency agreed with the IR data in Fig. 1.4. Consequently, the curing behavior of PF resin under steam-injection heating at 160°C seemed to be accompanied by a rapid breakdown of the ether linkage. With regard to the breakdown of the ether linkage, there are three possible pathways shown in Fig. 1.1. From the results of FT-IR and  $^{13}\text{C}$ -NMR of each heated resin, we could not confirm the products formed in

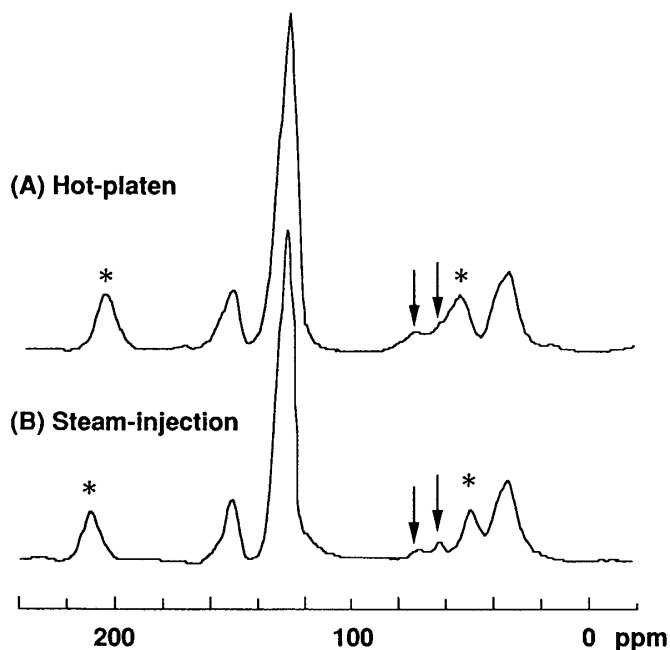


Fig. 1.5. 50.3 MHz CP/MAS NMR spectra of heated PF resin. Legend : (A) : Hot-platen heating at 160°C for 20 min, (B) : Steam-injection heating at 160°C for 20 min. Note : Asterisks indicate position of spinning sidebands.

Reactions (4) and (5). So, besides Reaction (1), it seemed that the curing reaction of resin under steam-injection heating may occur mainly as shown by Reaction (3).

(3) *Insoluble matter of steam-injection heated resin*

Figs. 1.6 show the result of extraction test with methanol on the resins heated by both heating methods. In the case of resin heated by hot-platen, the methanol insoluble matter gradually increased for 2 min and soon reached almost 100%, whereas rapid increase was observed for 1 min and then, constant to approximately 90% for the resin heated by steam-

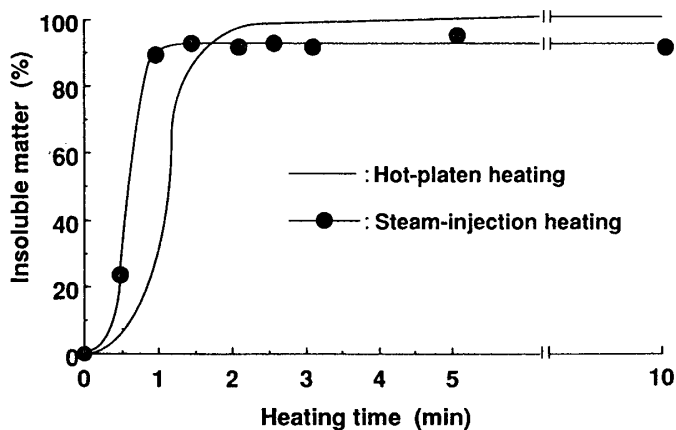


Fig. 1.6. Insoluble matter of PF resin during hot-platen heating and steam-injection heating at 160°C. Note : Solvent was methanol.

injection. These suggested that by steam-injection heating, PF resin reacts more quickly to grow methanol-insoluble matter than by hot-platen heating, and soon the curing reaction is inhibited.

### 1.2.3 Summary

The curing behavior of PF resin under high-pressure steam was studied using several analytical techniques. As heating time increased, curing reaction of 2-hydroxybenzyl alcohol under steam-injection heating may be followed by the formation and then breakdown of ether group. Under hot-platen heating, only the formation of ether groups was observed. The reaction of PF resin under steam-injection heating was accompanied by the rapid disappearance of ether group. Solvent extraction tests revealed that the methanol insoluble matter formed quickly under steam-injection heating. IR spectra of the methanol extract from steam-injection heated resin showed the formation of carbonyl groups which seemed to be derived from by-products. That is, at 160°C, PF resin immediately cured to some degree in the early stage because of the great heat capacity of steam. After that, however, the curing reaction was inhibited by the condensed water of steam and the by-products in heated resin.

## 1.3 Dynamic mechanical properties

### 1.3.1 Materials and methods

#### (1) Material

The aqueous PF resin used in this experiment is the same as described in section 1.2.1 (1).

#### (2) Preparation of specimen and pre-heating methods

A total of strip of glass fiber filter (ADVANTEC GA-200), measuring  $70 \times 8 \times 0.75$  mm (about 0.1 g), was dipped in a jar of PF resin in a brief time. Upon removal from the jar, the specimen was laid flat on a clean sheet of polytetrafluoroethylene and the excess resin was squeezed out uniformly. About 1 gram of resin was retained by each specimen.

The specimens were then pre-heated using hot-platen (in direct contact with upper and lower platens). The heating temperatures was 160°C, with heating times from 1 min to 120 min. After the specimen was heated for the scheduled time, it was dipped in liquid nitrogen in order to stop the curing reaction. Then, all the specimens were kept in a freezer set at -20°C.

In pre-heating using steam-injection, the specimens were held between two polytetrafluoroethylene, and were inserted into a thimble filter so as to prevent the resin from being washed out. The thimble filter containing the specimen was put into the reaction cell. Then, steam-injection heating was performed according to section 1.2.1 (2). The heating temperature at 160°C (steam pressure of 0.63 MPa) was used, with heating times ranging from 0.5 min to 20 min. The specimens were also kept in the freezer at -20°C.

## (3) DMA measurement

The frozen specimen was taken out of the refrigerator, and exposed to ambient temperature for 15 min. After that, DMA measurement was performed with RHEO VIBRON DDV-25FP instrument, scanning from 20°C to 220°C at a rate of 3°C/min and 10 Hz.

## 1.3.2 Results and discussion

## (1) Curing process of liquid PF resin

Fig. 1.7 shows the changes of dynamic mechanical properties during the curing process of liquid PF resin. The value of  $E'$  increased gradually in oven temperature up to 114°C ( $t_1$ ). After that, it increased dramatically until 135°C ( $t_2$ ), and soon reached a constant value. The values of  $E''$  and  $\tan \delta$  had peaks at 129°C and 123°C ( $T$ ), respectively. Fukuda *et al.*<sup>19)</sup> measured the curing process of dehydrated PF resol resin using torsional braid analysis (TBA). The behaviors of relative storage modulus (Gr) and logarithmic decrement obtained from the measurement indicated similar behaviors of  $E'$  and  $\tan \delta$  as shown in Fig. 1.7. According to Fukuda *et al.*<sup>19)</sup>, the point at which Gr began to increase rapidly (corresponding to  $t_1$  in Fig 1.7) was regarded as the gelation point of the resin. The stop point of the rapid increase in Gr (corresponding to  $t_2$ ) was regarded as the finishing point of resin curing reaction. The peak of logarithmic decrement (corresponding to  $T$ ) was regarded as the phase transition point during curing process.

In this study, as the PF resin solution contained about 54% of water (resin solid content about 46%), the mechanical curing process is considered to be affected by both the resin and water. The curing process of dried PF resin where water was excluded is shown in Fig. 1.8. The value of  $E'$  decreased slightly from the beginning of the measurement till about 55°C

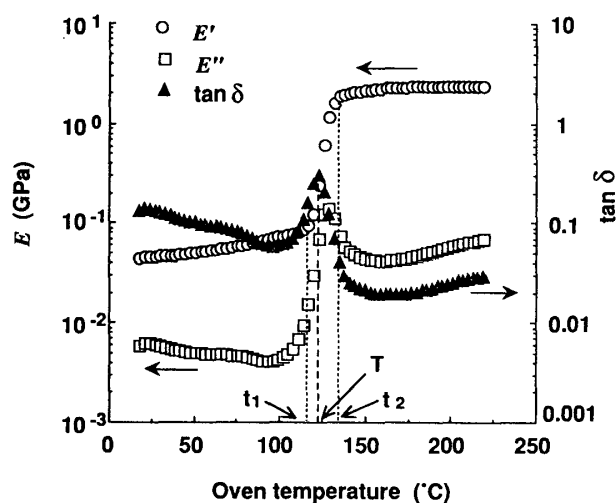


Fig. 1.7. Dynamic viscoelastic properties of PF resin observed at 3°C/min.  
Note:  $t_1$ : Gelation point,  $t_2$ : Finishing point of resin curing reaction,  
 $T$ : The phase transition point during curing process.

value of  $E'$  during measurement was probably due to the high  $E'$  of glass fiber filter specimen containing dried PF resin, even at room temperature. The  $E''$  and  $\tan \delta$  had broad peaks from 55°C to 138°C. It can be presumed that the marked curing reaction of PF resin itself takes place from 55°C to 138°C. Based on the above, the curing process of liquid PF resin in Fig 1.7 was analyzed as follows.

From 20°C up to 114°C ( $t_1$ ), the curing reaction took place with the formation of linear and short chains. However, as the PF resin has low molecular weight, and contained considerable amount of water at this stage, low values of  $E'$  and  $E''$  were recorded. From

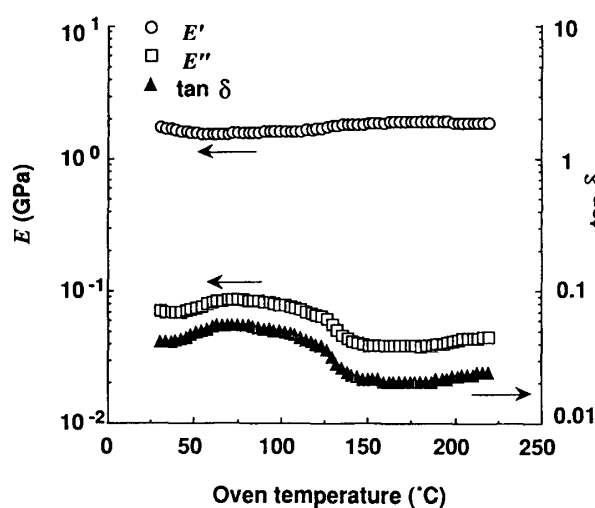


Fig. 1.8. Dynamic viscoelasticity of dried PF resin during scanning at 3°C/min and 10 Hz.

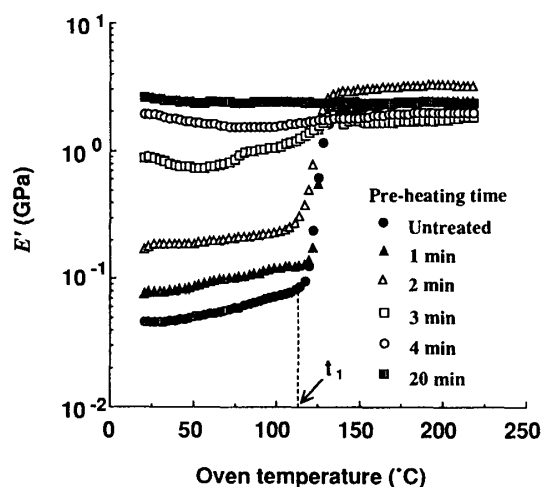


Fig. 1.9. Storage modulus ( $E'$ ) as a function of oven temperature at an increasing rate of 3°C/min, with a parameter of pre-heating time at 160°C of resin. Note:  $t_1$ : See Fig. 1.7.

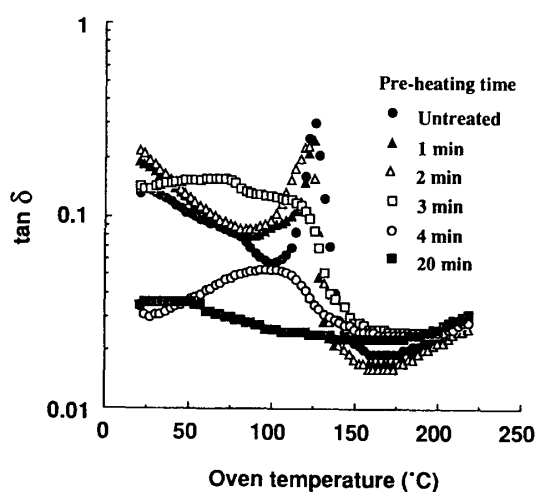


Fig. 1.10. Tan  $\delta$  as a function of oven temperature at an increasing rate of 3°C/min, with a parameter of pre-heating time at 160°C of resin.

114°C ( $t_1$ ) to 135°C ( $t_2$ ),  $E'$  and  $E''$  increased drastically. During this period, linear and branched chains continued to grow, and some of the branched chains could at the same time react locally together. In addition, marked evaporation of water took place. Katovlc *et al.*<sup>20)</sup> reported evaporation of water above 100°C in PF resin. Therefore, the gelation of the resin was thought to take place at this stage. Above 135°C, the value of  $E'$  was almost constant. PF resin was immobilized by further curing reaction. Thus, the structure changed to glassy state which retarded further reaction.

Fig. 1.9 shows the  $E'$  behaviors of PF resin samples pre-heated at 160°C using hot-platen for various duration. The values of  $E'$  at 20°C increased with increasing pre-heating time. That is, as the curing of PF resin and evaporation of water took place during pre-heating, the rigidity of pre-heated resin increased gradually. Fig. 1.10 shows the  $\tan \delta$  behaviors of PF resin samples pre-heated at 160°C using hot-platen for various duration. For both the 1- and 2-min samples,  $\tan \delta$  had sharp peak at about 120°C. As the pre-heating time became longer,  $\tan \delta$  peak broadened at lower temperatures and became low. For 20 min samples, since no peak value of  $\tan \delta$  was recorded, and the value of  $E'$  was almost constant during the DMA measurement, pre-heated resin was considered to have cured fully.

(2) *Curing behavior of resin pre-heated with hot-platen heating*

Generally, dynamic mechanical properties of wood adhesives are considered to have a significant influence on bonding performance. However, as wood adhesives are dissolved in solvents, the mechanical curing processes are affected by both resins and solvents. Therefore, calculation method for relative degree of mechanical cure involving the effect of solvents was investigated.

Fig. 1.11 shows the influence of pre-heating treatment on a typical  $E'$  behavior during DMA measurement at a constant heating rate. In the case of the untreated liquid resin (A), the  $E'$  value at the beginning of measurement (20°C) was the lowest. It increased gradually in lower oven temperature range. After that,  $E'$  dramatically increased and soon reached a constant value. In the case of the incompletely cured resin (B), it somewhat softened as the oven temperature increased, indicating a decrease of the  $E'$ . Following this, further curing reaction occurred, whereby  $E'$  eventually rose to a plateau. In the case of the fully cured resin (C), the value of  $E'$  was almost constant during the entire measurement because of the good thermostability of the resin. That is, when DMA measurement of pre-heated resin is performed from ambient temperature to elevated temperature at a constant heating rate, pre-heated resin would be finally cured completely at elevated temperature. The relative degree of mechanical cure achieved in pre-heated resin was measured based on the variation in  $E'$ , as discussed below.

The lowest  $\ln E'$  value of the untreated liquid resin at the beginning of DMA measurement (20°C) is represented by  $\ln E'_L$ . The highest  $\ln E'$  value of the untreated

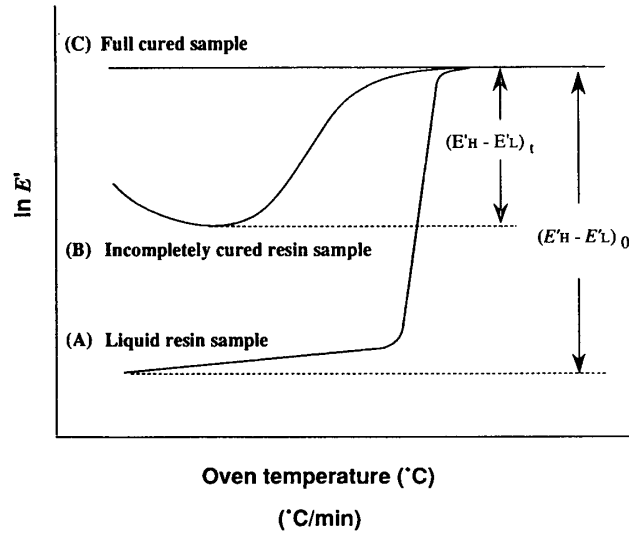


Fig. 1.11. Influence of pre-heating treatments on storage modulus curves.

resin at a elevated temperature is represented by  $\ln E'_H$ . The difference between  $\ln E'_H$  and  $\ln E'_L$  is expressed as :

$$(\ln E'_H - \ln E'_L)_0 = \ln (E'_H/E'_L)_0 \dots\dots\dots(1)$$

The expression in equation (1) indicates the ratio of the highest  $\ln E'$  and the lowest  $\ln E'$  during DMA measurement. Similarly, the lowest  $\ln E'$  value of the pre-heated resin at a low temperature is represented by  $\ln E'_L$ . The highest  $\ln E'$  value of the pre-heated resin at elevated temperature is represented by  $\ln E'_H$ . The difference between  $\ln E'_H$  and  $\ln E'_L$  is expressed as :

$$(\ln E'_H - \ln E'_L)_t = \ln (E'_H/E'_L)_t \dots\dots\dots(2)$$

The degree of mechanical cure achieved in the pre-heated resin is calculated from the following equation (3), which is derived from equations (1) and (2) :

$$\text{Dynamic mechanical curing index} = \frac{\ln (E'_H/E'_L)_0 - \ln (E'_H/E'_L)_t}{\ln (E'_H/E'_L)_0} \times 100 \dots\dots\dots(3)$$

where,

$$E'_H \geq E'_L$$

$E'_H$ : Maximum value of  $E'$  at high temperature

$E'_L$ : Minimum value of  $E'$  at low temperature

Suffix 0: Untreated

Suffix  $t$ : Pre-heating time

Fig. 1.12 shows the dynamic mechanical curing behavior of PF resin based on equation (3). The data of insoluble matter extracted with methanol, which is the conventional method, is shown in the same figure. In the case of the dynamic mechanical curing index, the value increased rapidly. The value reached 100 after 5 min, suggesting that resin heated for more than 5 min at 160°C was fully cured. In the case of the methanol

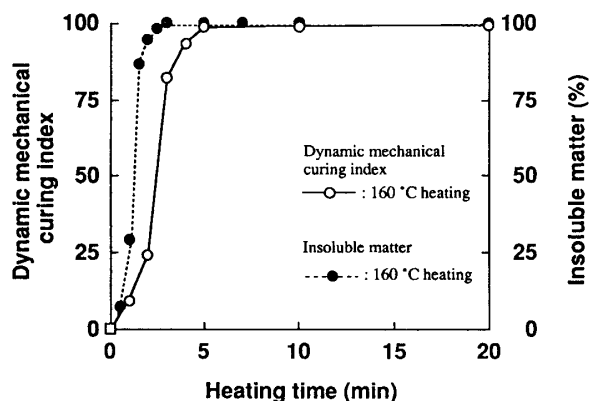


Fig. 1.12. Mechanical curing indexes and insoluble matter as functions of heating times. Note: The datas of insoluble matter were quoted from Figs. 1.6.

extraction, the insoluble matter at 160°C increased rapidly for 2 min and soon reached almost 100%. These results are slightly different from that of the dynamic mechanical curing index. The main reason could be due to the change in the size of insoluble matter which was related to the resin molecular size during the curing process. On the other hand, the dynamic mechanical curing index was related to the change of the  $E'$  of the resin sample containing water, during the curing process. In addition, this difference also seemed to be influenced by the extraction power of methanol. However, as described previously, dynamic mechanical properties of wood adhesives are considered to have a significant influence on bonding performance. Therefore, dynamic mechanical curing index appeared to be one of the useful methods to evaluate the degree of cure of resin.

(3) *Dynamic mechanical properties of resin pre-heated with steam-injection heating*

Fig. 1.13 shows the changes in the dynamic viscoelasticities for PF resin treated by steam-injection heating for various times at 160°C during temperature scans up to 220°C. The behavior of all the heated samples under steam-injection heating differed from those under hot-plate heating. As a whole,  $E'$  of steam-injection heated resin gave low value, comparing with that of hot-plate heated resin. The reason seems that the resin contained specimen took place swelling and dilution during steam-injection heating. In the sample pre-heated for 1 min, a slight increase in  $E'$  was observed at a lower temperature range (20–80°C), with steady increases in  $E''$  and  $\tan \delta$ . Above 80°C, further polymerization and crosslinking presumably occurred, whereby  $E'$  continued to rise gradually. The value of  $E''$  and  $\tan \delta$  decreased steadily when temperature rose up to 150°C and then somewhat increased. In other samples pre-heated for 5, 10, and 20 min,  $E'$  indicated slight decreases in thermal softening at lower temperatures. A slight increase in  $E'$  began at about 100°C while sudden dips of  $E''$  and  $\tan \delta$  were observed at the same temperature. The above phenomena might indicate considerable evaporation of the free water contained in the samples. That is, during the curing of PF resin under steam-injection heating, condensed



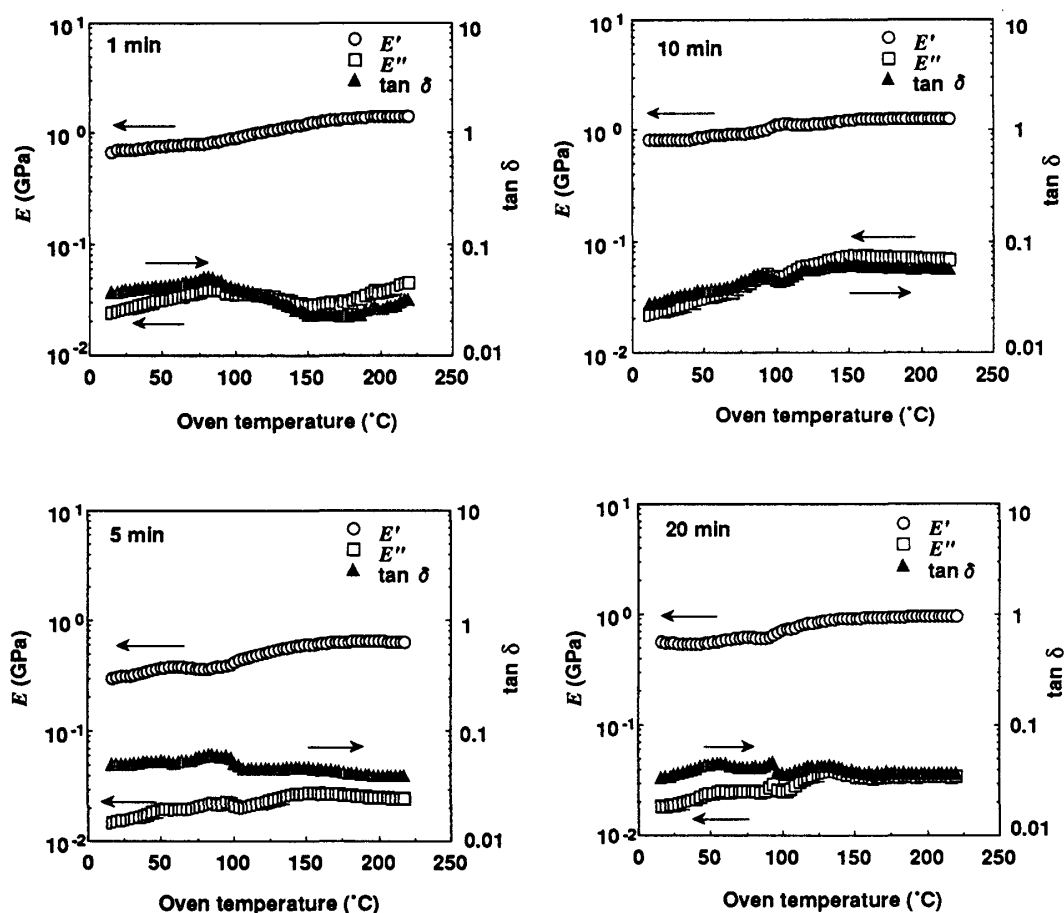


Fig. 1.13. Dynamic viscoelasticities of PF resin exposed to 160°C for various heating times during steam-injections.

water from steam and by-products from condensation reactions in PF resin might have been formed, and was confined in the sample due to the high-pressure steam. Thoman and Pearson<sup>7)</sup> suggested that polymerization of phenolic resin yielded water as a by-product and the additional water from condensation of steam shifts the chemical equilibrium, reducing the resin curing reaction. Gyevi *et al.*<sup>21)</sup> also reported that the by-products accumulated in a closed system could hinder the reaction of PF resin, and led to an equilibrium reaction. Consequently, the water arising from steam and a condensation reaction seemed to hamper the condensation reaction physically. Therefore, similar behavior might have been indicated by the dynamic viscoelasticity of steam-injected samples.

In all cases, it was revealed that the samples pre-heated under steam-injection has cured to some degree. The degree of mechanical curing was determined by calculating the dynamic mechanical curing index. The results are shown in Fig. 1.14. For the sample heated by hot-plate quoted from Fig. 1.12, the dynamic mechanical curing index increased gradually for 5 min and soon reached almost 100 i.e., fully cured, whereas in the sample heated by steam-injection, it rapidly increased for 1 min and then leveled off at

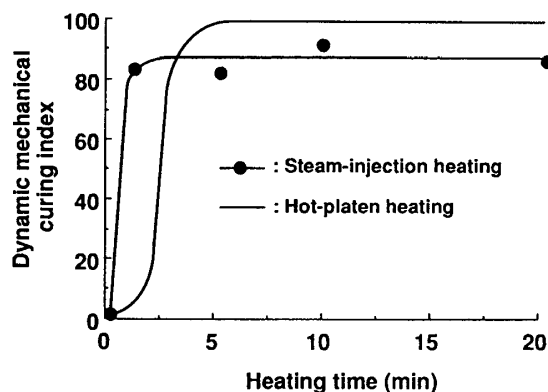


Fig. 1.14. Dynamic mechanical curing indexes for steam-injection heated and hot-platen heated PF resins as functions of heating time at 160°C.

approximately 85. These behaviors agreed with the results of methanol extraction tests shown in Fig. 1.6. It was also recognized that PF resin cured to some degree immediately in the early stage, and soon maintains a constant value under steam-injection heating. As for the relationship between moisture content and the degree of cure in PF resin, Chow and Mukai<sup>(6)</sup> pointed out that the degree of cure of the resin is directly related to the moisture content of the resin. Therefore, it can be concluded that steam-injection heating accelerates the curing reaction of PF resin to some degree in the early stage because of the great heat capacity of steam, but tends to hinder the curing reaction thereafter, due to the presence of water. It was for this reason that some free water was retained in PF resin heated under high-pressure steam, hence reducing the condensation reaction so as to decrease the collisions of functional-groups. Furthermore, by-products remained in the heated resin might also hinder the curing reaction.

### 1.3.3 Summary

The curing process of PF resin pre-heated with hot-platen and steam-injection was studied by DMA. The results and conclusion are summarized as follows: It appeared that the untreated liquid PF resin has a distinct gel point indicated by sudden changes of  $E'$ ,  $E''$ , and  $\tan \delta$ , whereas, dried PF resin exhibited different behaviors. As the pre-heating time was prolonged in hot-platen, there was a general increase in the initial (20°C)  $E'$ , followed by a drop of  $\tan \delta$  peak. It was also observed that the resin pre-heated for 5 min at 160°C cured completely with the disappearance of the  $\tan \delta$  peak. In addition, dynamic mechanical curing index which is a method of determining the degree of cure of resin in dynamic mechanical aspects was proposed. The method was considered to be one of the useful methods to evaluate the degree of resin cure. On the other hand, the dynamic viscoelasticity of steam-injected samples indicated similar behavior regardless of a heating time. Even in the resin pre-heated with steam-injection for 20 min at 160°C, a slight increase of  $E'$  began at 100°C, together with sudden dips of  $E''$  and  $\tan \delta$ . This could be due to the presence of considerable amount of free water in the samples. Based on the behavior

of dynamic mechanical curing index of steam-injected resin, it was recognized that the PF resin cured immediately to some degree in the early stage, and soon leveled off at a constant value.

## PART 2 Curing Behavior of Urea-Formaldehyde Resin under High-Pressure Steam

### 2.1 Introduction

As wood adhesives, UF resins have been commonly used for wood products using hot-pressing. However, in general, UF resins are less stable in humid conditions and at higher temperatures. Many researchers have studied the curings and degradations of UF resins using several analytical methods<sup>22-27</sup>.

As shown in Fig. 2.1, when the acidic hardening agents and the heat are added, UF resin rapidly becomes gels, producing a highly cross-linked insoluble polymer<sup>28</sup>. The formation of this polymer network is a consequence of the polyfunctional properties of urea whose four amide hydrogen atoms are capable of reacting with the hydroxyl groups of methylene glycol which is the hydrate of formaldehyde existing in an aqueous solution (Reaction 1). In the curing process, possible pathways of the reactions involve the formation of methylene bridges between the methylol and amide groups (Reaction 2). The formation of ether linkages between methylol groups also occurs (Reaction 3). In addition to the above reactions, the formation of uron expressed in Reaction 5 is confirmed. However, the curing reactions of UF resin are greatly affected by the molar ratio between

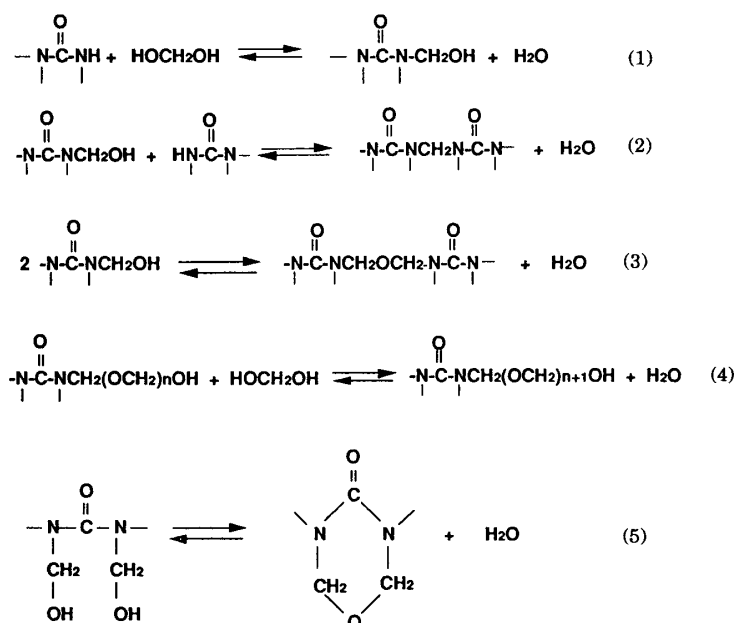


Fig. 2.1. Urea-formaldehyde polymelization and cure reaction.

urea and formaldehyde, kind of catalyst, pH of the resin solution, and temperature of the curing reaction. Consequently, the structure is still ambiguous.

The objective of this part is to reveal the curing behavior of UF resin under high-pressure steam both chemically and physically. The section 2.2 deals with the curing behavior of UF resin under high-pressure steam. That is, the UF resins heated by both heating methods were analyzed by FT-IR and solvent extraction.

The section 2.3 deals with the curing process and the effects of the pre-heating of UF resin under two heating methods measured by DMA. In addition, the dynamic mechanical curing behaviors of UF resin under each heating condition were investigated.

## 2.2 Chemical analysis of curing behavior

### 2.2.1 Materials and methods

#### (1) Materials

The UF resin was prepared by initially reacting 120 g of urea (U) with 324 g of formaldehyde solution (F), to give a F/U ratio of 2.0. The mixture was adjusted to a pH of 7.8–8.2 to have an alkaline solution, and then was heated while continuously stirring for 3.7 h at 85°C. In the course of this reaction, urea was added to bring the resin to a final F/U ratio of 1.7. The solution was then cooled and neutralized to pH 7.0. The resin properties obtained are shown in Table 2.1. The solution as well as the obtained UF resin had about 50 % solid content. Twenty percent (20%) ammonium chloride aqueous solution was added to the UF resin as a catalyst, at 1% based on solid resin weight prior to testing.

#### (2) Heating methods

Steam-injection heating and hot-platen heating were performed according to the section 1.2.1. The heating temperatures were 160°C (steam pressure of 0.63 MPa) and 120°C (steam pressure of 0.20 MPa) with heating times from 10 s to 20 min. After preparation, all the samples were kept in a freezer at  $-20^{\circ}\text{C}$ . The frozen samples were vacuum-dried and ground to a powder before analyses.

#### (3) FT-IR and solvent extraction

In FT-IR measurement, the infrared absorbance spectra were obtained on a Nihon

Table 2.1. Properties of UF resin.

pH	7.0
Viscosity (25°C)	0.04 (Pa·s)
Specific gravity (25°C)	1.180
Molecular weight ( $\bar{M}_n$ )	595
Gelation time (25°C)	50 (min)
Non-volatile component (105°C, 3 h)	50 (%)

Legend:  $\bar{M}_n$ : Number average molecular weight. Note: Molecular weight ( $\bar{M}_n$ ) obtained from polyethylene glycol calibration curve of gel permeation chromatography.

Bunko FT-IR 7000 using the KBr pellet technique.

In solvent extraction measurement, heat treated and pulverized (less than 20 mesh) a dry sample weighing 2.0 g was extracted for 3 h with warm water at 60°C. Then, the amount of the residue was determined, and the ratio of insoluble matter was calculated.

## 2.2.2 Results and discussion

### (1) Curing behavior of UF resin examined by FT-IR

Fig. 2.2 shows the infrared spectral changes of UF resin under hot-plate heating (A) and steam-injection heating (B) at 160°C. These measurements were made after heating the samples at 160°C for 1 min (a), 5 min (b) and 20 min (c), respectively. In hot-plate heating (A), besides a decrease of the absorption intensity of the band at 1,020–1,025  $\text{cm}^{-1}$ , slight increases of the absorption intensity of the bands at 1,500–1,520  $\text{cm}^{-1}$ , 1,290–1,300  $\text{cm}^{-1}$  and at about 810  $\text{cm}^{-1}$  were observed with increasing heating time. However, dramatic changes did not occur because UF resin rapidly formed highly crosslinked polymer at higher temperature of 160°C.

On the other hand, with steam-injection heating (B), marked changes occurred in the spectra during heating. That is, absorption of the band at about 1,540–1,560  $\text{cm}^{-1}$  was missing, and only a strong absorption of the band at about 1,500–1,520  $\text{cm}^{-1}$  appeared with increasing heating time. Strong absorption of the band at about 1,290–1,300  $\text{cm}^{-1}$  also appeared. The absorption intensity of the band at about 1,020–1,025  $\text{cm}^{-1}$  decreased, and the absorption of the band at 810  $\text{cm}^{-1}$  was observed clearly.

These absorption bands was assigned as shown below<sup>29,30</sup>; 1,540–1,560  $\text{cm}^{-1}$  for

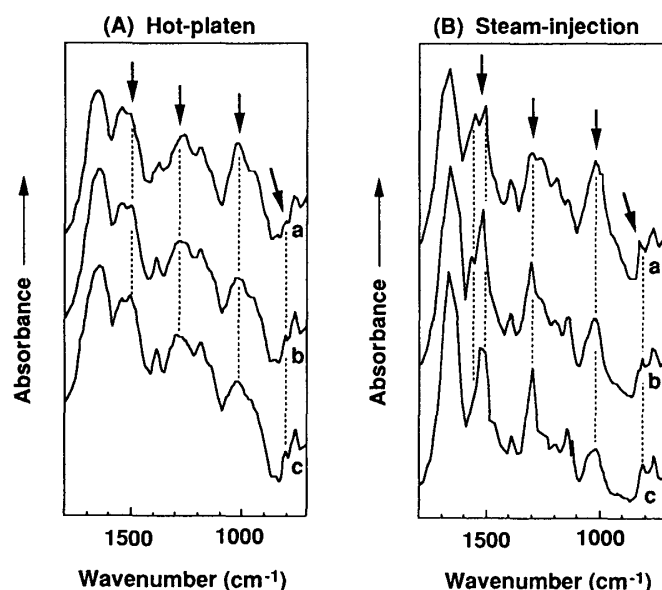


Fig. 2.2. Infrared spectra of UF resin during hot-plate heating (A) and steam-injection heating (B) at 160°C. Legend : (a) 1 min, (b) 5 min, (c) 20 min.

secondary, linear amide;  $1,500\text{--}1,520\text{ cm}^{-1}$  for linear or cyclic tertiary amide;  $1,290\text{--}1,300\text{ cm}^{-1}$  for OH and/or tertiary cyclic amide;  $1,020\text{--}1,025\text{ cm}^{-1}$  for  $\text{CH}_2\text{OH}$ ;  $810\text{ cm}^{-1}$  for COC linkages of a uronic ring.

Some researchers<sup>29,31,32)</sup> tried to observe changes in functional groups during the curing of UF resin by using obtained infrared spectra data. That is, some of the infrared spectra were quantified on the same relative basis by normalizing the measured absorbances using the carbonyl (at about  $1,650\text{ cm}^{-1}$ ) peak as the criterion in each spectrum. To examine the curing behavior of the resin quantitatively, as well as to compare the heated resins treated by the two heating methods with each other, the relative normalized absorbances described above were calculated for each spectrum.

Fig. 2.3 shows the plot of changes in these absorbance against heating times on hot-platen heated (A) and steam-injection heated (B) UF resin at  $160^\circ\text{C}$ . In a hot-platen heating (A), the absorption intensity of the band at  $1,540\text{--}1,560\text{ cm}^{-1}$  decreased slightly, whereas the absorption intensity of the band at  $1,500\text{--}1,520\text{ cm}^{-1}$  increased immediately

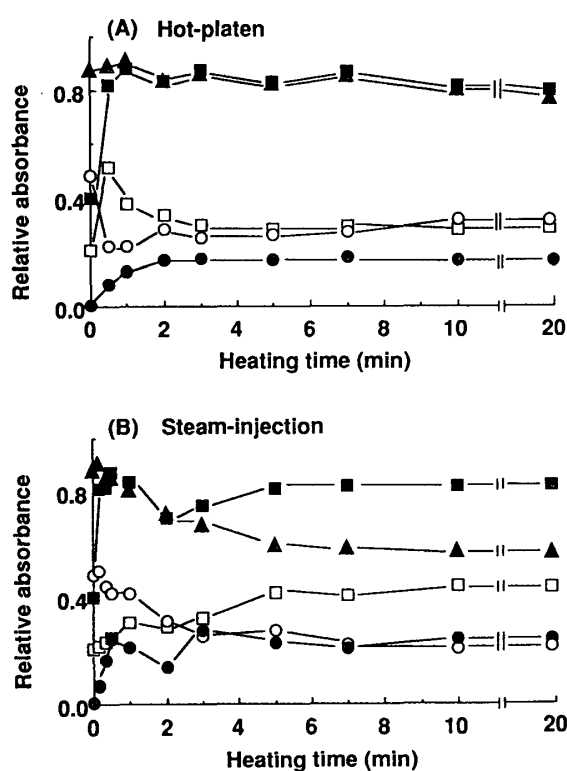


Fig. 2.3. IR spectral changes of UF resin during hot-platen heating (A) and steam-injection heating (B) at  $160^\circ\text{C}$ .  
Legend: ▲:  $1,540\text{--}1,560\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ■:  $1,500\text{--}1,520\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , □:  $1,290\text{--}1,300\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ○:  $1,020\text{--}1,025\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ●:  $810\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ .

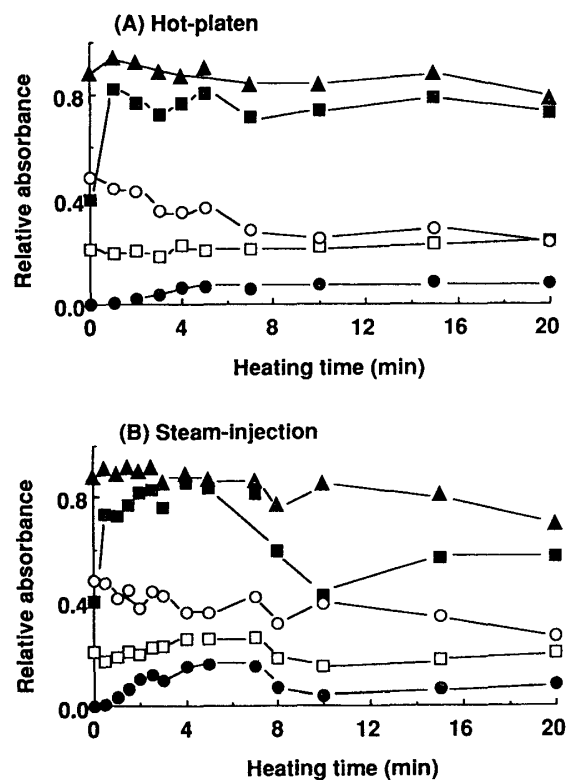


Fig. 2.4. IR spectral changes of UF resin during hot-platen heating (A) and steam-injection heating (B) at  $120^\circ\text{C}$ .  
Legend: ▲:  $1,540\text{--}1,560\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ■:  $1,500\text{--}1,520\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , □:  $1,290\text{--}1,300\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ○:  $1,020\text{--}1,025\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ , ●:  $810\text{ cm}^{-1}/1,650\text{ cm}^{-1}$ .

after heating and level off soon. The absorption intensity of the band at  $1,290\text{--}1,300\text{ cm}^{-1}$  increased and reached a maximum in 30 s, followed by a considerable decrease. The absorption intensity of the band at  $1,020\text{--}1,025\text{ cm}^{-1}$  decreased soon after treatment and then had a slight increase afterwards. Furthermore, the band at  $810\text{ cm}^{-1}$  began to appear immediately after the heating and level off after 2 min of the treatment. In a steam-injection heating (B), the absorption intensity of the band at  $1,540\text{--}1,560\text{ cm}^{-1}$  decreased slowly, whereas the absorption intensity of the band at  $1,500\text{--}1,520\text{ cm}^{-1}$  increased immediately after heating, and then decreased slightly for 2 min, then increased again gradually. The absorption intensity of the band at  $1,290\text{--}1,300\text{ cm}^{-1}$  increased continuously, whereas the absorption intensity of the band at  $1,020\text{--}1,025\text{ cm}^{-1}$  decreased gradually over the entire heating time. In addition, the absorption intensity of the band at  $810\text{ cm}^{-1}$  appeared and increased up to 30 s, slightly decreased at 2 min, and then somewhat increased. As observed, marked chemical changes seemed to occur within about 2 min in steam-injection heated UF resin.

Fig. 2.4 also shows the plots of changes in some of these absorbance against heating times of hot-platen heated (A) and steam-injection heated (B) UF resin at  $120^{\circ}\text{C}$ . In a hot-platen heating (A), the changes of each absorbance were more slow against heating times than those done at  $160^{\circ}\text{C}$ . In a steam-injection heating (B), the absorption intensity of the band at  $1,540\text{--}1,560\text{ cm}^{-1}$  decreased slowly, whereas the absorption intensity of the band at  $1,500\text{--}1,520\text{ cm}^{-1}$  increased significantly at the first stage of heating, decreased largely from 5 min to 10 min heating, and then increased gradually. On the other hand, the absorption intensity of the band at  $1,290\text{--}1,300\text{ cm}^{-1}$  increased continuously and slightly for 7 min, decreased slightly, and then somewhat increased. The absorption intensity of the band at  $1,020\text{--}1,025\text{ cm}^{-1}$  decreased slightly over the entire heating time. Furthermore, the absorption intensity of the band at  $810\text{ cm}^{-1}$  showed a similar behavior to that of the band at  $1,290\text{--}1,300\text{ cm}^{-1}$ . In this case, marked chemical changes seemed to occur at about 10 min.

Judging from the above, during hot-platen heating of UF resin, tertiary amide grew rapidly accompanied by the consumption of a hydroxyl group, and a uronic ring also seemed to form. These changes were considered to be due to processes such as Reactions (2), (3), (5) of Fig. 2.1 in the forward direction. Similarly, in the steam-injection heating of UF resin, it seemed that the curing reactions occurred rapidly after heating and the UF resin cured to some degree. On the other hand, based on the temporary decrease of tertiary amide (at  $1,500\text{--}1,520\text{ cm}^{-1}$ ) and the continuous decrease of secondary amide (at  $1,540\text{--}1,560\text{ cm}^{-1}$ ), the UF resin appeared to be partly decomposed such as a hydrolysis and so on. Generally, during hydrolysis, Reactions (1) and (4) will occur in the reverse direction. They will be accompanied by the reverse of (2) and (3), and succeeded by the loss of methylol as in (1) and (4)<sup>28)</sup>. However, it was thought that cyclic ether, such as a

uronic ring formed by a curing reaction, was relatively stable even under steam-injection heating.

(2) *Insoluble matter of steam-injection heated resin*

Figs. 2.5 and 2.6 show the results of the extraction tests with warm water at 60°C on the resins heated by each heating method at 120°C and 160°C, respectively. In the case of resin heated by hot-platen heating at 120°C in Fig. 2.5, the insoluble matter increased gradually up to 10 min and reached almost 100%, whereas for the resin heated by steam-injection, a rapid increase of the insoluble matter was observed for 1 min and then kept constant reaching approximately 68%. These observations suggested that in steam-injection heating at 120°C, the UF resin reacts more quickly to grow warm water insoluble matter than that in hot-platen heating because of supply of heat energy from steam. However, at a later time, the curing reaction seemed to be hindered by water contained in the resin. In this case, the reactions of UF resin were apparently considered to come to an equilibrium. This behavior was similar to that of PF resin under steam-injection heating at 160°C as described in Part 1<sup>33)</sup>.

In Fig. 2.6, irrespective of heating methods, the insoluble matter rapidly increased for a few seconds. After that, in hot-platen heating, the value approached 100%. In steam-injection heating, it decreased gradually with increasing heating time. It can be presumed that under steam-injection heating at 160°C the UF resin rapidly cured to some degree in the early stage. However, in general, the UF resin under wet conditions at higher temperatures is less stable. Therefore, hydrolysis would occur which was caused by water included in the resin uncured yet, and by the condensed water from steam. Thus, water soluble matter of low-molecular weight seemed to increase as heating time increased.

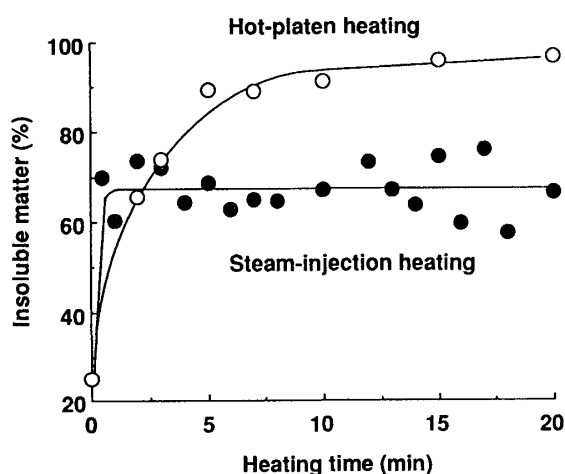


Fig. 2.5. Insoluble matter of UF resin during hot-platen heating and steam-injection heating at 120°C. Note: Solvent was warm-water (60°C).

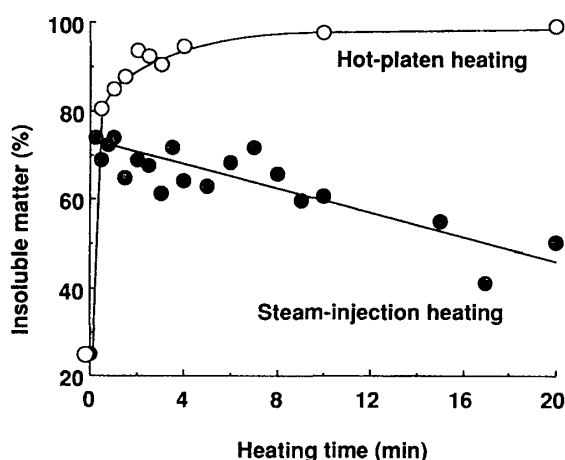


Fig. 2.6. Insoluble matter of UF resin during hot-platen heating and steam-injection heating at 160°C. Note: Solvent was warm-water (60°C).



### 2.2.3 Summary

The curing behavior of UF resin under high-pressure steam was studied using FT-IR and solvent extraction. The results were as follows :

1) In the reaction of UF resin under steam-injection heating, marked chemical changes took place, which were not observed in the hot-plate heating. Furthermore, the cyclic ether formed by the curing reaction was considered to be relatively stable even under steam-injection heating.

2) Compared with hot-plate heating, UF resin reacted more quickly and warm water insoluble matter increased in steam-injection heating. Afterwards, however, it was shown that the curing reaction of UF resin appeared to come to an equilibrium state at 120°C, and the hydrolysis tended to occur at 160°C.

## 2.3 Dynamic mechanical properties

### 2.3.1 Materials and methods

#### (1) Material

The UF resin used in this experiment is the same as described in section 2.2.1 of this part. Twenty percent (20%) ammonium chloride aqueous solution was added to the resin as a catalyst at 1% based on solid resin weight before specimen preparation.

#### (2) Preparation of specimens and pre-heating methods

The specimens were prepared by soaking strips (70×8×0.75 mm) of glass fiber filter in the resin solution before the pre-heating treatment. Dried specimens were prepared by vacuum-drying using a desiccator. The detailed specimen preparation procedure and pre-heating methods were described 1.3.1 (2).

In pre-heating method using hot-plate, the heating temperatures were 120°C and 160°C with heating times from 0.5 to 10 min. In pre-heating method using steam-injection, the heating temperatures were 160°C (steam pressure of 0.63 MPa) and 120°C (steam pressure of 0.20 MPa) with heating times from 0.5 to 20 min.

#### (3) DMA measurement

DMA was performed with a RHEO VIBRON DDV-25FP instrument, scanning from 20°C to 220°C at a rate of 3°C/min and 10 Hz.

### 2.3.2 Results and discussion

#### (1) Curing process of liquid UF resin

Fig. 2.7 shows the changes of dynamic mechanical properties during the curing process of liquid UF resin using ammonium chloride as a catalyst. A double distinct sigmoidal shape having the changing points of  $T_0$  and  $T_2$  was observed in the  $E'$ . Generally, thermosetting materials, particularly wood adhesives, undergo two significant changes such as gel transition and glass transition during the curing process. However, as wood adhesives are dissolved in solvents, the mechanical curing processes are considered to be

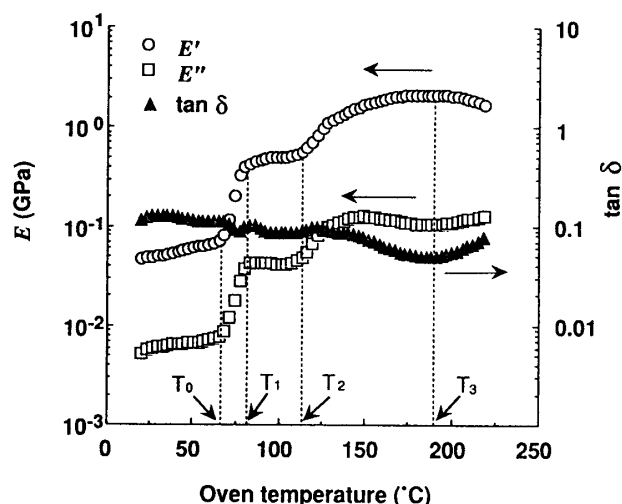


Fig. 2.7. Dynamic viscoelastic properties of UF resin during the curing process observed at 3°C/min intervals and at 10 Hz.

affected by both the resins and the solvents. In particular, water release occurs during the curing period in aqueous condensation resin, which may cause a phase change in the resin.

Toussaint *et al.*<sup>34)</sup> measured the curing process of epoxy resin with isothermal DMA measurements, and also obtained the same behavior of  $E'$  and  $E''$  as shown in Fig. 2.7. They fully discussed this curing process in its morphological aspect. Stuligross and Koutsky<sup>24)</sup> reported on the morphological structure of uncured and cured UF resins. They proposed that the curing of UF resin proceeds via crystallization and agglomeration.

Based on the above references, the curing process of liquid UF resin in Fig. 2.7 was analyzed. From the beginning of measurement up to  $T_0$  (about 73°C), as the UF resin was in a liquid state, low values of  $E'$  and  $E''$  were observed. In this stage, the resin molecules moved relatively freely in water. The slight increases of the values of  $E'$  and  $E''$  were mainly considered to be caused by the evaporation of some of the water. From  $T_0$  to  $T_1$  (about 80°C), the values of  $E'$  and  $E''$  increased drastically. During this period, a marked curing reaction of the UF resin appeared to take place, and the movement of the resin molecules was restricted remarkably. Some researchers<sup>22,35-37)</sup> observed that the curing reaction of UF resin with ammonium chloride usually began to take place at below 100°C. From  $T_1$  to  $T_2$  (about 116°C), very little or no variation of the  $E'$  and  $E''$  values were observed. This result may be attributed to the formation of aggregates or a branched or linear extending chain occurring from some of the microgels of the resin. If this union suddenly increases the molecular weights, its influence on the mean molecular weight between crosslinks is very small<sup>34)</sup>. Consequently, the influence on the  $E'$  which depends on the said formation was considered to be reduced. In this stage, however, as some water still appeared to be present in the specimen, it was also necessary to take into account its effects on the  $E'$  values to some degree. From  $T_2$  to  $T_3$  (about 188°C), violent evaporation of water appeared to take place

at  $T_2$ . Chow *et al.*<sup>31)</sup> reported that the evaporation of water above 100°C occurred for UF resin. Furthermore, the numbers, sizes, and shapes of the aggregates, as well as the dimensions of the other growing macromolecules and the degrees of conversions, were such that they reacted with each other. As a result, the structure of the UF resin was immobilized and change to a glassy state. After completion of curing, the resin began to decompose at about  $T_3$  as indicated by the decreasing of the  $E'$ .

(2) *Dynamic mechanical properties of resin pre-heated with hot-platen heating*

Fig. 2.8 shows the  $E'$  behaviors of UF resin samples after pre-heating at 120°C for various times with hot-platen heating. For these samples, the values of  $E'$  at 20°C increased with increasing pre-heating time. For the 30-s pre-heated sample, as the oven temperature increased, the value of  $E'$  continued to increase up to about 150°C. After that, the  $E'$  eventually attained to a "plateau" value. It appeared that the 30-s pre-heated resin did not cure so much, and considerable water was still contained in the sample. The 1-min pre-heated sample softened somewhat as the oven temperature increased, indicating a decrease in the  $E'$  at about 50°C. Following this, further polymerization and crosslinking presumably occurred, whereby the  $E'$  eventually rose to a plateau. For the 5-min pre-heated sample, even though the oven temperature increased, the sample did not softened so much. After that, the  $E'$  eventually reached a plateau. As the resin pre-heated for 10 min had been fully cured, the  $E'$  of the sample almost maintained a constant value or decreased slightly because of some decomposition of the resin during the measurement.

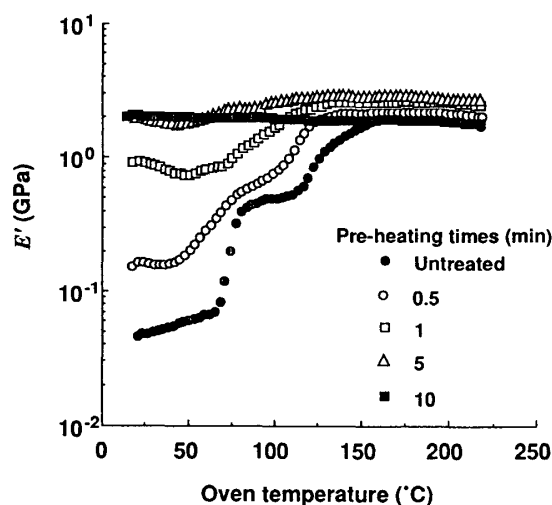


Fig. 2.8. Storage modulus ( $E'$ ) of UF resin after exposure to 120°C for various heating times with hot-platen heating.

In case of heating at 160°C, similar  $E'$  behaviors were obtained. However, the resin pre-heated for 3 min was considered to have fully cured because the  $E'$  had an almost constant value during the entire measurement.

(3) *Dynamic mechanical properties of resin pre-heated with steam-injection heating*

Fig. 2.9 shows the  $E'$  behavior of the resin after pre-heating at 120°C for various heating times with steam-injection heating. Compared to Fig. 2.8, each curing process of the resin with pre-heating times was very different. In Fig. 2.9, irrespective of pre-heating times, each  $E'$  at 20°C had almost the same value, and the  $E'$  curves during measurements were similar to each other, indicating the temporary decrease in  $E'$  values up to 100°C. Judging from these behavior of  $E'$ , each steam-injection heated resin was considered to cure to some degree regardless of the heating time. However, it was thought that UF resin did not cure

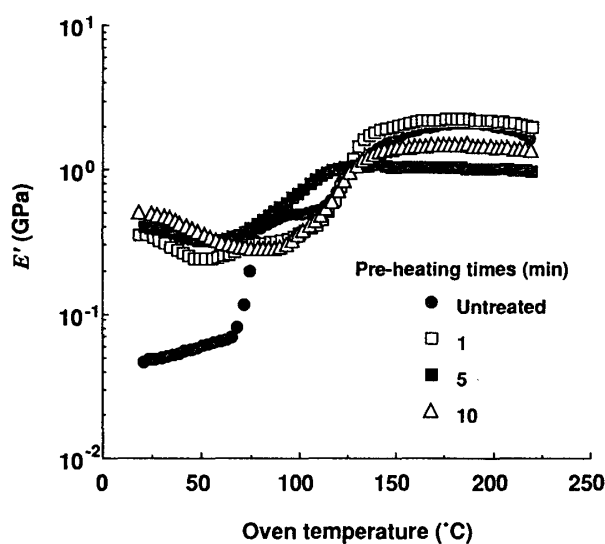


Fig. 2.9. Storage modulus ( $E'$ ) of UF resin after exposure to 120°C for various heating times with steam-injection heating.

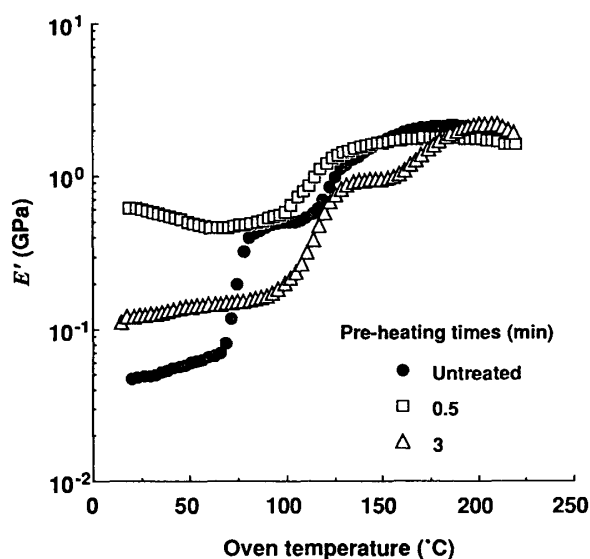


Fig. 2.10. Storage modulus ( $E'$ ) of UF resin after exposure to 160°C for various heating times with steam-injection heating.

completely with steam-injection heating at 120°C even at longer heating times.

Fig. 2.10 shows the  $E'$  behavior of resin after pre-heating at 160°C for various heating times with steam-injection heating. For the 30-s pre-heated sample, the value of  $E'$  decreased to some extent and then increased with increasing oven temperature. This result revealed that resin pre-heated under this condition cured to some degree. Prior to DMA measurement, the UF resin sample under the above conditions was slightly rigid which was thought to have contributed to the above result. However, for the resin sample pre-heated for 3 min, the value of  $E'$  at 20°C was lower than that of the sample pre-heated for 30 s. The value of  $E'$  continued to increase without showing a temporary decrease until 100°C with increasing oven temperature. In fact, the sample state before measurement was very soft and wet. Consequently, as steam-injection time increased, UF resin was considered to cure to some degree and then return to a liquid state.

The dynamic mechanical curing behavior of UF resin under steam-injection heating was investigated using the mechanical curing index as described in 1.3.2 (4). The results are shown in Fig. 2.11. For the sample pre-heated at 120°C, the index increased gradually for 5 min, followed by a slight decrease with increasing heating time. For the sample pre-heated at 160°C, the index rapidly increased for 30 s, and then decreased immediately until it reached a 0 value after about 5 min. According to the result of the section 2.2, UF resin rapidly cured to some degree in the early stage. Afterwards, however, the reaction of the resin apparently came to equilibrium at 120°C, and hydrolysis gradually took place at 160°C. This result was slightly different from that of the dynamic mechanical curing index in this study. This was the reason why the dynamic curing mechanical index was calculated from the change of the  $E'$  of the sample which includes not only the resin but also water. Therefore, we came up with the following conclusion: in the heating temperature

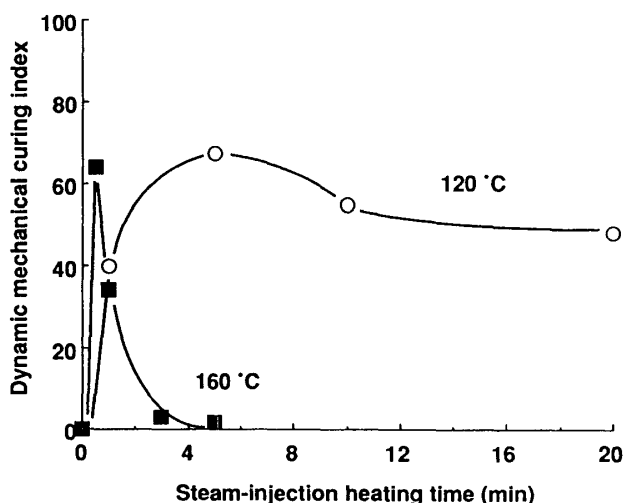


Fig. 2.11. Dynamic mechanical curing indexes for steam-injection heated UF resin as functions of steam-injection times.

at 120°C, UF resin gradually cured to some degree in the early stage. Afterwards, although the curing reaction apparently came to equilibrium, the resin was slightly diluted by the by-products from the condensation reaction of the resin and the condensed water from steam. In the heating temperature at 160°C, the resin rapidly cured to some degree in the early stage. Subsequently, the resin rapidly returned to a liquid state because of the occurrence of decomposition such as hydrolysis and dilution of the resin with condensed water. That is, from a mechanical viewpoint as well, it was suggested that the curing behavior of UF resin under steam-injection heating differs much from that under hot-platen heating.

### 2.3.3 Summary

The mechanical curing process of UF resin treated under several conditions was studied using DMA. The following results were obtained:

- 1) The curing process of liquid UF resin with catalyst proceeded through a two-stage curing process with increasing oven temperature.
- 2) The cured states of resins pre-heated by hot-platen heating and steam-injection heating were observed. In addition, a dynamic mechanical curing index was calculated to reveal the dynamic mechanical curing behaviors under steam-injection heating. It was found that under steam-injection heating, UF resin immediately cured to some degree, and then, dilution and/or decomposition took place.

## PART 3 Bonding Performances of Wood Adhesives under High-Pressure Steam

### 3.1 Introduction

In the previous parts, the curing behavior and mechanical properties of several wood adhesives under high-pressure steam using a special reaction cell were discussed. In this part, the effects of additives and steam-injection time on the bonding strengths of PF resin and UF resin adhesives were investigated. In addition, the suitable bonding conditions of these resins under high-pressure steam were developed.

### 3.2 Bonding strength of PF resin

#### 3.2.1 Materials and methods

##### (1) Materials

The same aqueous PF resol resin as described in the section 1.2.1 (1) was used in this experiment. Wheat flour and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) used as PF resin additives were supplied from Oshika Shinko Co. Ltd. The glue preparation and their properties are shown in Table 3.1. Rotary peeled lauan (*Shorea* spp.) veneer with a thickness of 1.3 mm was used. The air-dry density and the moisture content of veneers were 0.56 g/cm<sup>3</sup> and 8.9%, respectively.

##### (2) Manufacture of plywood and measurement of bonding strength

In steam-injection pressing of plywood, it is difficult to get steam penetrate in between

Table 3.1. Preparations and properties of PF glue.

PF resin (phr)	100	100	100	100
Wheat flour	—	15	—	15
Sodium carbonate	—	—	2	2
Viscosity at 25°C (Pa·s)	0.1	3.5	0.38	4.65
Gelation time at 135°C (min)	13.27	11.75	8.02	11.75

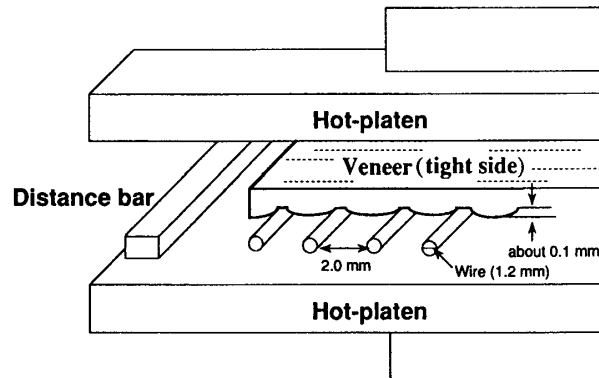


Fig. 3.1. Production method of grooved veneer. Note: The veneer was pressed for 40 s using hot-platen at 160°C.

the veneers. Therefore, grooves were set by hot-pressing in the face veneers as shown in Fig. 3.1. The amount of the glue applied to the core veneer was 180 g/m<sup>2</sup>. 3-ply plywood with the dimensions of 30×80×3.5 mm were prepared using a specially designed pressing apparatus as shown in Fig. 3.2. The specimens were subjected to press pressure of 0.3 MPa exerted by a pair of springs. The apparatus containing the specimen was then put into the reaction cell<sup>33)</sup> for steam-injection heating. Steam-injection heating was performed according to the section 1.2.1 (2). The heating temperature was 160°C (steam pressure of 0.63 MPa) with heating time of 1–10 min. After the apparatus containing the specimen

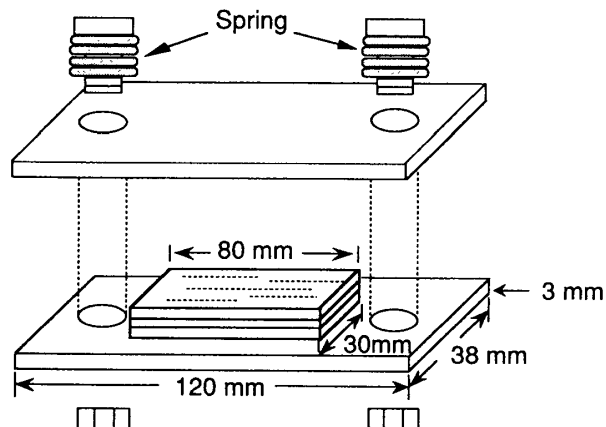


Fig. 3.2. Production of 3-ply plywood using a specially designed pressure apparatus.

was heated for the scheduled duration, it was taken out and cooled by dipping in liquid nitrogen. As a control plywood, 3-ply plywood was also prepared using untreated veneers. The apparatus containing the specimen were heated in the oven at 160°C. In order to cure the resin completely, a heating time of 30 min was applied. The specimens were then cooled using similar method as steam-injection heated samples.

Intermittent steam-injection heating, that is ; steam is exhausted temporarily before the saturated high pressure steam fill in the reaction cell, then, steam is injected again for short period, was investigated. In this study, steam-injection heating for 1 min ; steam exhausting from the reaction cell for 30 s ; and steam-injection heating for 1 min, was applied.

The prepared 3-ply plywoods were conditioned at 20°C and 65% relative humidity for a week. Test specimens were prepared according to JIS (Japan Industrial Standard) K6802. After a cyclic boiling treatment (soaking in boiling water for 4 h ; drying at 60°C for 20 h ; soaking in boiling water for 4 h ; cooling and testing in the wet state), the tensile shear bonding strength was measured. The total of six test specimens were used for each fabricating condition. The average value and standard deviation were calculated for each condition.

### (3) *Measurement of glue line temperature*

During steam-injection heating, the temperature in the glue line of 3-ply plywood was measured by inserting the copper-constantan thermocouples (wire diameter of 0.1 mm) into the center of the core veneer. The thermocouples were connected to a data processor via a data-logger, and the temperatures were recorded at a time interval of 5 Hz.

### 3.2.2 *Results and discussion*

#### (1) *Effects of additives and steam-injection time on bonding strength*

The tensile shear bonding strengths of 3-ply plywood after cyclic boiling were tested by varying the additives and steam-injection time. The results are shown in Figs. 3.3–3.6. The percentages of wood failure in these 3-ply plywoods were, in general, low. This could be due to the considerably low pressing pressure exerted by the specially designed pressure apparatus. In the case of 3-ply plywood glued with a neat glue (only PF resin), the bonding strength decreased markedly with increasing steam-injection time (Fig. 3.3). The maximum average value of the bonding strength was achieved in a steam-injection time of 1 min, which was almost the same as that of the control plywood. The bonding strength of the glue extended with a wheat flour also decreased markedly with increasing steam-injection time (Fig. 3.4). In addition, these bonding strengths were very weak compared to that of the control plywood. In the case of 3-ply plywood glued with the sodium carbonate added glue (Fig. 3.5), the average value of the bonding strength at 1 min was comparable to that of the 3-ply plywood glued with a neat glue at 1 min (Fig. 3.3). However, the bonding strength was increased with increasing steam-injection time, and the average values of



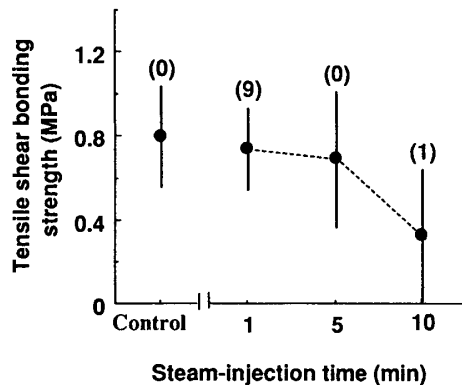


Fig. 3.3. Effect of steam-injection (160°C) duration on wet bonding strength of 3-ply plywood glued with a neat PF glue. Legend: Control: Oven heating for 30 min at 160°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

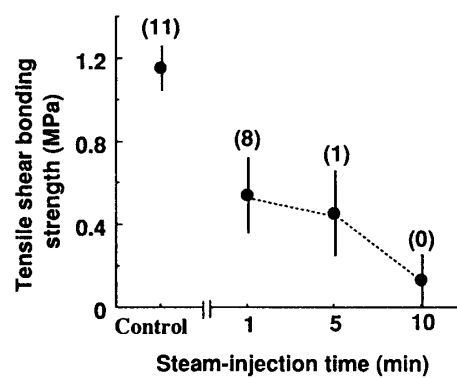


Fig. 3.4. Effect of steam-injection (160°C) duration on wet bonding strength of 3-ply plywood glued with a wheat flour extended PF glue. Legend: Control: Oven heating for 30 min at 160°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

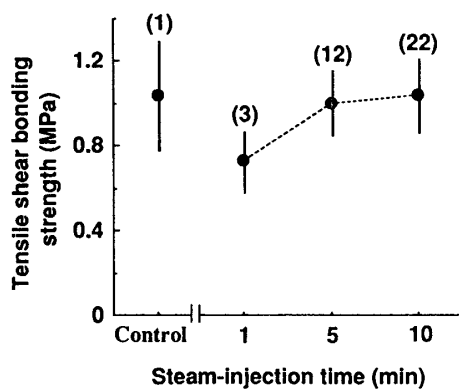


Fig. 3.5. Effect of steam-injection (160°C) duration on wet bonding strength of 3-ply plywood glued with a sodium carbonate added PF glue. Legend: Control: Oven heating for 30 min at 160°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

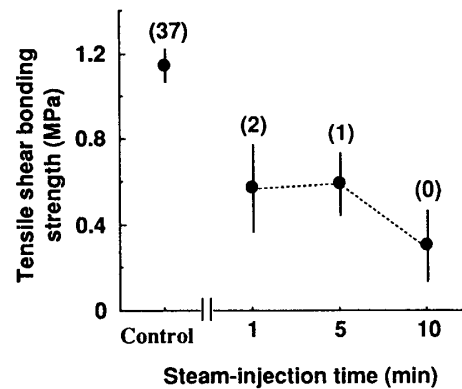


Fig. 3.6. Effect of steam-injection (160°C) duration on wet bonding strength of 3-ply plywood glued with a wheat flour and sodium carbonate added PF glue. Legend: Control: Oven heating for 30 min at 160°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

bonding strength at 5 min and 10 min were nearly the same as that of control plywood. The lower bonding strength of glue added with a wheat flour and sodium carbonate were registered compared to that of the control plywood (Fig. 3.6). Though the bonding strengths at 1 min and 5 min were almost the same, the value at 10 min was relatively lower.

During the wood-composite manufacturing process using conventional hot-pressing, the bonding strength of PF resin generally impose with progressing curing reaction.

Therefore, when heating time is prolonged at elevated temperature, the bonding strength should increase. In this study, however, except in the case of the sodium carbonate added glue, the opposite trend was observed. According to the result of Part 1, PF resin immediately cures to some degree in a few minutes because of the great heat capacity of high pressure steam at 160°C. After that, PF resin maintains apparently a certain curing situation under steam-injection heating at 160°C. Thus, the decreases of the bonding strength with increasing steam-injection time, as shown in Figs. 3.3, 3.4 and 3.6 were not due to the reaction such as decomposition of the resin, but possibly due to over-penetration and dilution of the liquid PF resin by high-pressure steam<sup>38,39)</sup>. In general, extender such as wheat flour controls the viscosity and moisture content of the glue, hence reduces the glue line failure resulting from drying out or over-penetration<sup>40)</sup>. Therefore, it was natural that the bonding strength of control plywood glued with wheat flour extended glue was stronger than that of control plywood glued with a neat glue under oven heating (Figs. 3.3, 3.4 and 3.6). However, in 3-ply plywood prepared under steam-injection heating, the overall bonding strengths in the case of using wheat flour extended glue were somewhat weaker than those of using a neat glue. The one of the reason seems to be that the resin amount in wheat flour extended glue was less than that of a neat glue. Sodium carbonate is known to be an accelerator for curing alkaline PF resin<sup>41)</sup>. As shown in Table 3.1, the addition of sodium carbonate into the resin shortens the gelation time. Though gelation time does not appear to relate directly to resin performance<sup>42)</sup>, the faster gelation of the resin would promote the rapid formation of glue line. The rapid formation of glue line in early stage under steam-injection heating seemed to result in an increase of bonding strength with increasing steam-injection time.

(2) *Changes in glue line temperature*

To investigate the cause of decreasing the bonding strength with increasing steam-injection time, temperature behavior of the glue line with a neat glue in the manufacture of

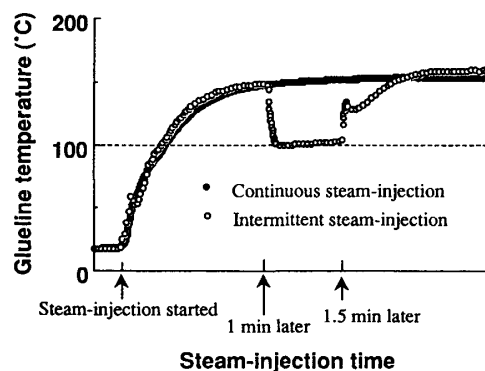


Fig. 3.7. Temperature behavior of glueline of 3-ply plywood with a neat PF glue under continuous and intermittent steam-injection heating at 160°C.

3-ply plywood during steam-injection heating was observed. The result is shown in Fig. 3.7. When steam was injected continuously, the temperature of the glue line rose rapidly for about 1 min and then gradually reached a constant. That is, the temperature of the glue line well reached the curing temperature of the resin in 1 min.

Therefore, the decrease of the bonding strength with increasing steam-injection time could be explained as follows. In the early stage of steam-injection heating, evaporation of water and the curing reaction of PF resin in glue line took place to a certain extent because of the great heat capacity of steam. After that, however, as the saturated high pressure steam filled in the reaction cell, the further curing reaction was inhibited<sup>33)</sup>. PF resin was reported to perform poorly under high moisture condition<sup>43)</sup>. In addition to this, it is well known that excessive moisture in wood and/or glue could increase penetration by maintaining a low viscosity and facilitating resin flow<sup>44)</sup>. Consequently, PF resin seemed to swell in moisture in a long steam-injection heating. Dilution and/or over-penetration of resin could have also occurred, together with the decrease of cohesive forces of resin. These could lead to the development of starved joint in the glue line, resulting in the reduced bonding strength.

### (3) *Improvement of bonding strength*

Judging from the above results, intermittent steam-injection heating was considered to be effective for improvement of the bonding strength. Fig. 3.7 shows the temperature behavior of glue line under the intermittent steam-injection heating. When steam was injected into the reaction cell for 1 min, the temperature of the glue line rose rapidly to about 150°C. During this period, the evaporation of water in the glue line was expected to take place because saturated high pressure steam did not filled in the reaction cell yet. Furthermore, the PF resin seems to become cured and solid to some degree as described in Part 1. After that, as soon as steam was exhausted, the temperature of the glue line fell down to 100°C. However, the temperature was maintained at 100°C for 30 s. That is, even if steam was exhausted temporarily, the temperature of the glue line was maintained at 100°C under atmospheric pressure. Therefore, the retention of the resin without swelling, dilution and over-penetration as well as evaporation of water were expected. When steam was injected again, the temperature also rose rapidly. The bonding strength without causing starved joint in the glue line is expected to improve owing to the further curing reaction of the resin.

Fig. 3.8 shows the bonding strengths of the 3-ply plywood glued with various PF glue preparation in intermittent steam-injection heating. When a neat glue and sodium carbonate added glue were used, the bonding strengths were improved dramatically in short heating time. In sodium carbonate added glue, the time required to develop the bonding strength was only one-fourth that of continuous steam-injection heating time. The average values exceeded 1 MPa, which was similar to those of control plywood as shown in Figs. 3.3

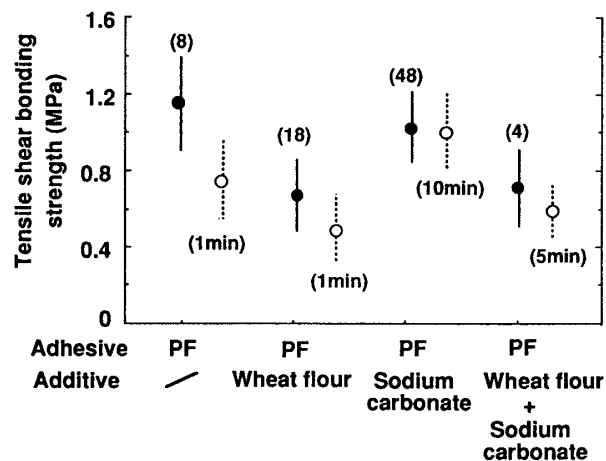


Fig. 3.8. Bonding strength of 3-ply plywood glued with various PF glue preparation under intermittent steam-injection heating at 160°C. Legend: —●—: Intermittent steam-injection heating, ---○---: Maximum values of continuous steam-injection heating as shown in Figs. 3.3–3.6. Note: Steam-injection schedule: injection for 1 min, exhausting pressure for 30 s and injection for 1 min.

and 3.5. The wood failure in sodium carbonate added glue showed relatively high value. Steiner *et al.* reported the effectiveness of accelerating resin gelation on bonding of higher-moisture content wood<sup>45)</sup>. The bonding strength of the glue extended with wheat flour was also improved, but to a lesser extent. The average value was considerably lower than that of control plywood as shown in Figs. 3.4 and 3.6. Thus, the proportion of wheat flour in the glue appeared to be inadequate for the improvement of bonding strength in steam-injection heating.

### 3.2.3 Summary

The effects of additives and steam-injection time on bonding strength of PF resin under high-pressure steam were studied. The suitable bonding condition of PF resin under high-pressure steam was also developed. The results were summarized as follows. The bonding strengths of 3-ply plywood with a neat PF glue and wheat flour extended PF glue after cyclic boiling treatment decreased with increasing steam-injection time. With sodium carbonate added glue, the bonding strength increased gradually with increasing steam-injection time. To improve the bonding strength in short heating time, intermittent steam-injection heating, that is, steam-injection heating for 1 min; steam exhausting for 30 s; and

Table 3.2. Preparations and properties of UF glue.

UF resin (1% NH <sub>4</sub> Cl) (phr)	100	100
Wheat flour	—	25
Viscosity at 25°C (Pa·s)	0.05	5.2
Gelation time at 100°C (min) (Boiling water)	1.93	3.05

finally steam-injection heating for 1 min was tried. The bonding strengths of a neat glue and sodium carbonate added glue were improved dramatically. In both cases, the average values of the bonding strength exceeded 1 MPa.

### 3.3 Bonding strength of UF resin

#### 3.3.1 Materials and methods

##### (1) Materials

The UF resin used in this experiment is the same as described in section 2.2.1 (1). Twenty percent (20%) ammonium chloride aqueous solution as a catalyst, was added to the resin at 1 % based on solid resin weight. Wheat flour as UF resin additive was supplied from Oshika Shinko Co. Ltd. The glue preparation and the properties are shown in Table 3.2. The veneer used in this experiment is also the same as described in section 3.2.1 (1).

##### (2) Manufacture of plywood and measurement of bonding strength

The grooved veneers were also used for faces so as to be able to get steam penetrate in between the veneers. The amount of the glue applied to the core veneer was  $165.6 \text{ g/m}^2$ . The detailed preparation procedure of 3-ply plywood using the reaction cell was performed according to 3.2.1 (2). Considering the results of Part 2, the heating temperature was  $120^\circ\text{C}$  (steam pressure of 0.2 MPa) with heating time of 30 s to 5 min. Control plywood was also prepared by curing the resin of the specimen contained in the apparatus into the oven at  $120^\circ\text{C}$  for 20 min. Intermittent steam-injection heating, that is, steam-injection heating for 1 min; steam exhausting from the reaction cell for 30 s; and steam-injection heating for 1 min, was also applied. The temperature behavior of the glue line with wheat flour extended UF glue in preparation of 3-ply plywood under the intermittent steam-injection heating was observed.

The prepared 3-ply plywood were tested immediately in order to prevent the after cure of the resin. Test specimens were prepared according to JIS (Japan Industrial Standard) K6801. After the accelerated deterioration treatment (immersing in warm water at  $60^\circ\text{C}$  for 3 h), the tensile shear bonding strengths were measured. The six test specimens were used for each condition. The average value and standard deviation were calculated for each condition.

##### (3) Measurement of glue line temperature

The glue line temperature during steam-injection heating were measured according to the sections 3.2.1 (3).

#### 3.3.2 Results and discussion

##### (1) Effects of additives and steam-injection time on bonding strength

Fig. 3.9 shows the bonding strength of 3-ply plywood glued with UF glue (only UF resin). The average value of the bonding strength increased gradually with increasing steam-injection time. However, the bonding strengths, even at 5 min, were very weak

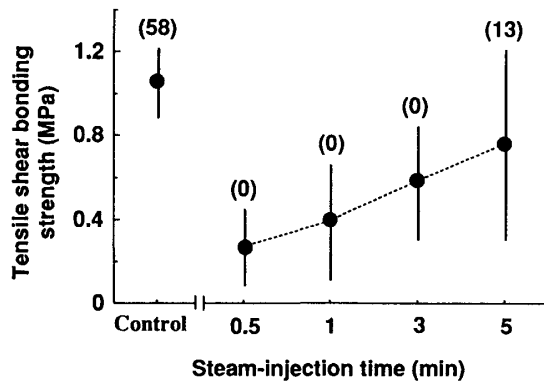


Fig. 3.9. Effect of steam-injection (120°C) duration on bonding strength of 3-ply plywood glued with UF resin. Legend: Control: Oven heating for 20 min at 120°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

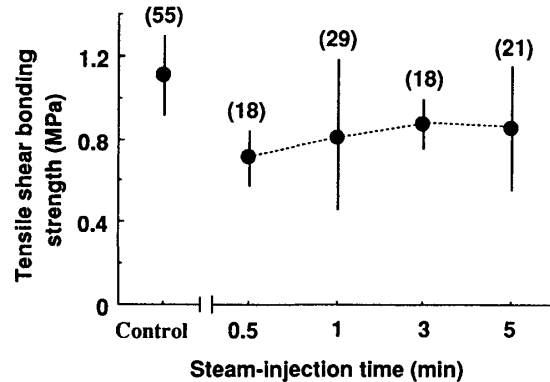


Fig. 3.10. Effect of steam-injection (120°C) duration on bonding strength of 3-ply plywood glued with wheat flour extended UF resin. Legend: Control: Oven heating for 20 min at 120°C. Note: The figures in the parentheses show the average values of the percentage of wood failure.

compared to that of the control plywood. The percentages of wood failure in these 3-ply plywoods were extremely low compared to that of the control plywood. According to the result of Part 2, UF resin cures to some degree in a few minutes. Then, the resin is slightly diluted by by-products from the condensation reaction of the resin and the condensed water from steam, though the curing reactions apparently come to equilibrium. Therefore, the development of the bonding strength under steam-injection heating seems to be due to proceeding the curing reaction heterogeneously and slowly.

Fig. 3.10 shows the bonding strength of 3-ply plywood glued with wheat flour extended UF glue. The bonding strengths of wheat flour extended glue were almost same values in spite of steam-injection time. However, these bonding strengths were also weak compared to that of the control plywood. Therefore, regardless of steam-injection time and of addition of wheat flour, the bonding strength yielded under steam-injection heating was found to be rather poor.

## (2) Changes in glue line temperature

To investigate the cause of poor bonding strength under steam-injection heating, temperature behavior of the glue line in preparation of 3-ply plywood with wheat flour extended glue was observed. The result is shown in Fig. 3.11. When steam was injected continuously, the temperature of the glue line rose rapidly to more than 100°C for about 1 min and then gradually reached a constant value. It was found that the glue line temperature was sufficient to take place the curing reaction of the resin.

Therefore, the poor bonding strength with steam-injection heating could be explained as follows. In the early stage of steam-injection heating, evaporation of water as well as the

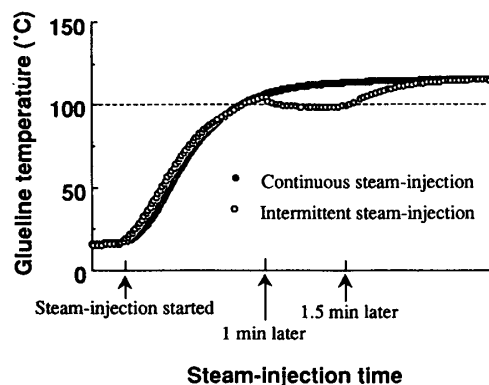


Fig. 3.11. Temperature behavior of glueline of 3-ply plywood with wheat flour extended UF glue under continuous and intermittent steam-injection heating at 120°C.

curing reaction of UF resin in glue line took place to a certain extent because of the great heat capacity of steam. However, as the saturated high pressure steam was filled in the reaction cell, the further curing reaction was inhibited as described in Part 2<sup>46)</sup>. Evaporation of water in the glue line also inhibited. It is well known that excessive moisture causes aqueous resins to penetrate into veneer during hot-pressing, often resulting in resin depletion in the glue line and subsequent poor bonding performance<sup>47)</sup>. Consequently, in addition to the inhibition of curing reaction of UF resin, swelling, dilution and over-penetration could have occurred in a long steam-injection heating. These could lead to the development of starved joint in the glue line, hence resulting in poor bonding strength. The bonding strength glued with wheat flour extended UF glue showed relatively higher value than that of glued with UF glue under steam-injection heating. This appeared to be that the addition of wheat flour reduced penetration of resin. Incidentally, the changes of the bonding strength of UF glue with increasing steam-injection time were different from that of PF glue as described in the section 3.2.2 (1). The reasons were considered to be due to low steam pressure and short heating time.

### (3) Improvement of bonding strength

Judging from the above results, as with the previous section 3.2, intermittent steam-injection heating was considered to improve the bonding strength. Fig. 3.11 shows the temperature behavior of glue line under intermittent steam-injection heating. When steam was injected into the reaction cell for 1 min, the temperature of the glue line rose rapidly to more than 100°C. Evaporation of water in the glue line was expected to take place during this period because saturated high pressure steam did not filled in the reaction cell yet. The curing reaction of UF resin also seemed to proceed to some degree during this period. After that, as soon as steam was exhausted, the temperature of the glue line fell to about 100°C and then, the temperature was maintained for 30 s. In glue line, the retention of the resin as well as evaporation of water was expected for this period. When steam was injected again,

the temperature also rose. The bonding strength seemed to improve owing to the further curing reaction of the resin without causing starved joint in the glue line.

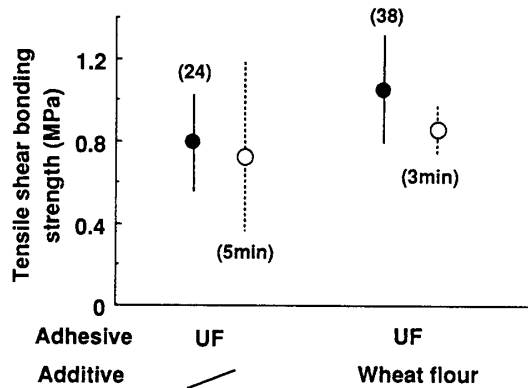


Fig. 3.12. Bonding strength of 3-ply plywood glued with two UF glue preparations under intermittent steam-injection heating at 120°C. Legend: —●—: Intermittent steam-injection heating, ---○---: Maximum values of continuous steam-injection heating as shown in Figs. 3.9 and 3.10. Note: Steam-injection schedule: injection for 1 min, exhausting pressure for 30 s and injection for 1 min.

Fig. 3.12 shows the bonding strengths of the 3-ply plywood glued with UF glue and wheat flour extended UF glue in intermittent steam-injection heating. These bonding strengths were improved dramatically in short heating time. The average values exceeded 1 MPa. When UF glue was used, the bonding strength was also improved, but to a lesser extent. The reason seemed that over penetration and dilution of resin in glue line take place even under intermittent steam-injection heating. Thus, in addition to intermittent steam-injection heating, the addition of additive such as wheat flour into the glue was necessary for development of the bonding strength of UF resin under steam-injection heating.

### 3.3.3 Summary

To reveal the bonding performance of UF resin under high-pressure steam at 120°C, the effects of additive and steam-injection time on bonding strength were studied. Based on the results obtained, the suitable bonding conditions of UF resin under high-pressure steam was investigated. The results were summarized as follows. When UF glue was used, the bonding strength after immersing in warm water at 60°C for 3 h increased gradually with increasing steam-injection time. When wheat flour extended glue was used, the bonding strengths were almost the same values in spite of steam-injection time. However, these bonding strengths were poor. To improve the bonding strength in short heating time, intermittent steam-injection heating was tried. When wheat flour extended glue was used, the bonding strength was improved dramatically, and the average values exceeded 1 MPa.



## Conclusion

This paper consists of three parts covering 1) curing behavior of PF resin under high-pressure steam, 2) curing behavior of UF resin under high-pressure steam, 3) bonding performances of PF and UF resins under high-pressure steam. The results of each part are summarized as follows:

1) The curing behavior of PF resin under high-pressure steam was investigated by comparing with that under hot-plate heating. From chemical points of view, analyses using FT-IR,  $^{13}\text{C}$ -NMR and solvent extraction were conducted and the results obtained were as follows; The curing reaction of 2-hydroxybenzyl alcohol, as a model compound, under steam-injection heating at  $160^\circ\text{C}$  was followed by rapid formation and then breakdown of the ether group. By steam-injection heating at  $160^\circ\text{C}$ , the PF resin immediately cured to some degree, and in a few minutes after, it maintained an equilibrium situation seemingly. The steam-injection heated resin also resulted in the rapid disappearance of the ether group.

From a physical point of view, the effects of hot-plate pre-heating treatments on the dynamic thermomechanical properties of PF resin used in this study were investigated in detail using DMA. It appeared that the untreated liquid PF resin had a distinct gel point with sudden changes of  $E'$ ,  $E''$ , and  $\tan \delta$ , during DMA measurement. As the pre-heating time was prolonged, the  $E'$  at  $20^\circ\text{C}$  generally increased with a decrease in the  $\tan \delta$  peak. It was also observed that the resin pre-heated for 5 min at  $160^\circ\text{C}$  cured completely with the disappearance of the  $\tan \delta$  peak. In addition, mechanical curing index which is a method of evaluating the degree of resin cure in dynamic mechanical aspect was proposed.

In the case of sample steam-injection heated for 20 min at  $160^\circ\text{C}$ , a slight increase in  $E'$  was observed at above  $100^\circ\text{C}$  while sudden decrease in the  $E''$  and  $\tan \delta$  also were observed at around  $100^\circ\text{C}$ . The reason seemed to be that condensed water from steam and by-product from condensation reaction of PF resin had been absorbed and retained in the sample due to the high-pressure of the steam. Using dynamic mechanical curing index, the curing behavior of PF resin under steam-injection heating was investigated. It was recognized that PF resin cured to some degrees in its early stage, and the curing leveled off within short time.

2) The curing behavior of UF resin under high-pressure steam was investigated by comparing with that under hot-plate heating. From a chemical point of view, analyses using FT-IR, and solvent extraction were performed and the results obtained were as follows. In the reaction of UF resin under steam-injection heating, linear or cyclic tertiary amides and cyclic ethers were obtained. Furthermore, marked chemical changes took place. In the steam-injection heating, UF resin reacted more quickly to be converted to a warm water-insoluble matter than the case of hot-plate heating because of the great heat

capacity of the steam. However, it was shown that the reaction of UF resin apparently came to equilibrium at the lower temperature of 120°C, and the hydrolysis tended to occur at the higher temperature of 160°C with increasing heating time. This suggested that the condensed water from steam and the by-product from the condensation reaction of UF resin were absorbed and retained in the resin. Furthermore, evaporation of water included in the untreated resin seemed to be also inhibited by high-pressure steam.

From physical point of view, the effects of hot-plate pre-heating (at 120 or 160°C) treatments on the dynamic thermomechanical properties of UF resin used in this study were investigated in detail using DMA. The curing of liquid UF resin with ammonium chloride was found to proceed through a two-stage process with increasing oven temperature. As the pre-heating time became longer, regardless of the heating temperature, the behavior of  $E'$  on DMA measurement changed from a double sigmoidal shape to an almost constant one. However, in pre-heating with steam-injection at 120°C, regardless of the pre-heating time,  $E'$  curves during measurements became similar to each other. In the case of pre-heating with steam-injection at 160°C for 30 s,  $E'$  curves was similar to those obtained for hot-plate heated for a few minutes. However, the  $E'$  curve became similar to that of liquid resin with increasing pre-heating time at 160°C. Based on the behavior of the dynamic mechanical curing index, the UF resin under steam-injection heating was thought to cure immediately to a certain degree. Then, the resin was considered to be slightly diluted by condensed water or by-product at 120°C, or degraded to return back to gel and/or a liquid state at 160°C.

3) To realize the bonding performances for PF and UF resins under high-pressure steam, the effects of additive and steam-injection time on bonding strength which is measured after a accelerated deterioration treatment were investigated. In addition, the optimum bonding conditions under high-pressure steam were discussed. In PF resin, as steam-injection heating time increased at 160°C, the bonding strengths of 3-ply plywood glued with a neat PF glue and wheat flour extended PF glue decreased. Starved joint in glue line was believed to have taken place under steam-injection heating when the heating time increased. In the case of 3-ply plywood glued with sodium carbonate added glue, the bonding strength increased gradually with increasing steam-injection time.

In order to improve the bonding strength in short heating time, intermittent steam-injection heating was performed; that is, steam was exhausted intermittently before the saturated high pressure steam was filled in the reaction cell and then steam was injected again for short period. The bonding strengths of a neat PF glue and sodium carbonate added PF glue were improved dramatically in a short heating time. The average values of the wet bonding strength exceeded 1 MPa, similar to those of control plywood. The bonding strength of wheat flour extended glue was also improved to some degree but to a lesser extent. It was clarified that the intermittent steam-injection heating improved the bonding strength of PF resin under steam-injection heating.

In UF resin, as steam-injection heating time increased at 120°C, the bonding strengths of 3-ply plywood glued with UF glue increased gradually and the one glued with wheat flour extended UF glue revealed similar bonding value. However, these bonding strengths were low when compared with that of the control plywood prepared under oven heating. Starved joint in glue line was believed to have taken place under the steam-injection heating, similar to the case of PF glue. In order to improve the bonding strength, the intermittent steam-injection heating was performed in the same manner as the case of PF glue. When wheat flour extended glue was used, the bonding strengths were improved dramatically in short heating times. The average values of the bonding strengths exceeded 1 MPa. When the neat UF glue was used, the bonding strength was also improved to a certain degree but to a lesser extent. Therefore, in the case of the UF resin, it was made clear that the addition of wheat flour into the glue and the use of intermittent steam-injection heating were effective for the improvement of bonding strength of UF resin under steam-injection heating.

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